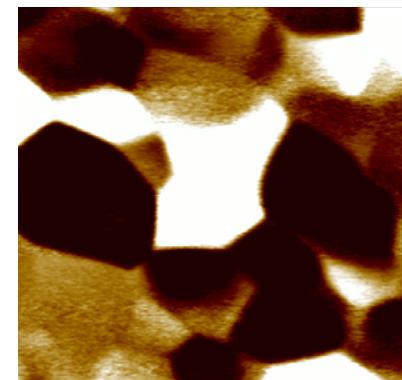
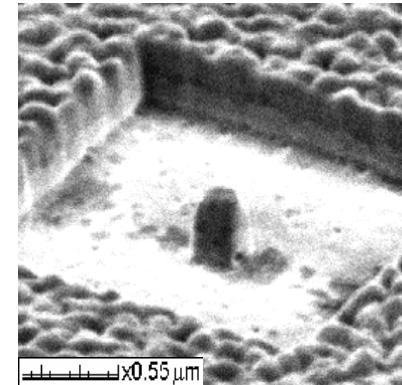
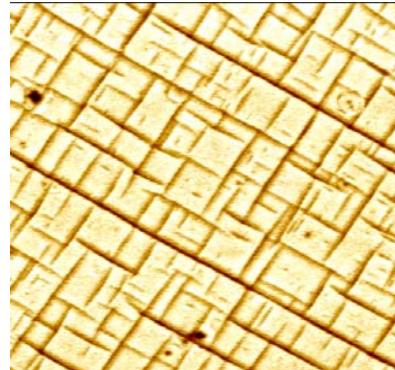
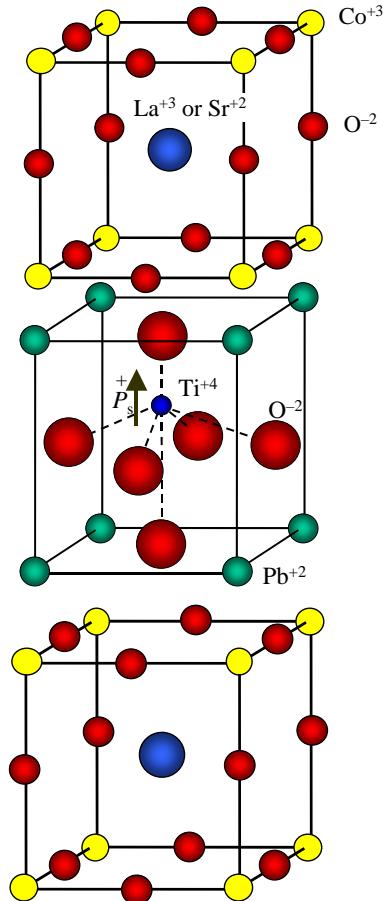


# Science and Technology of Complex Oxides



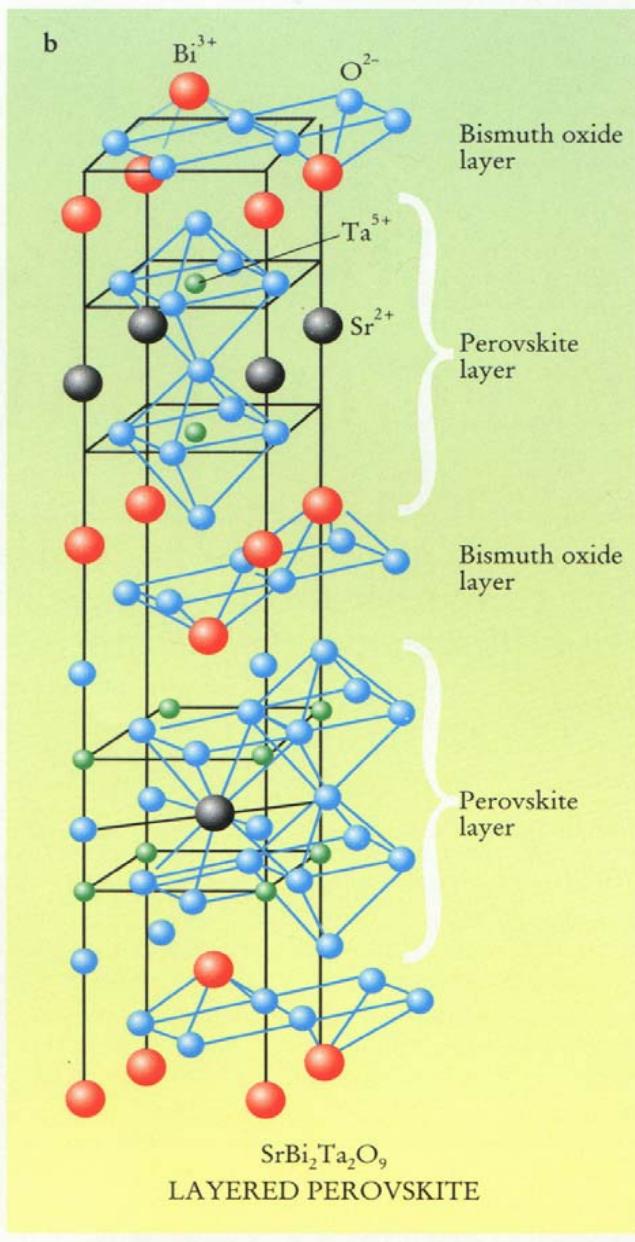
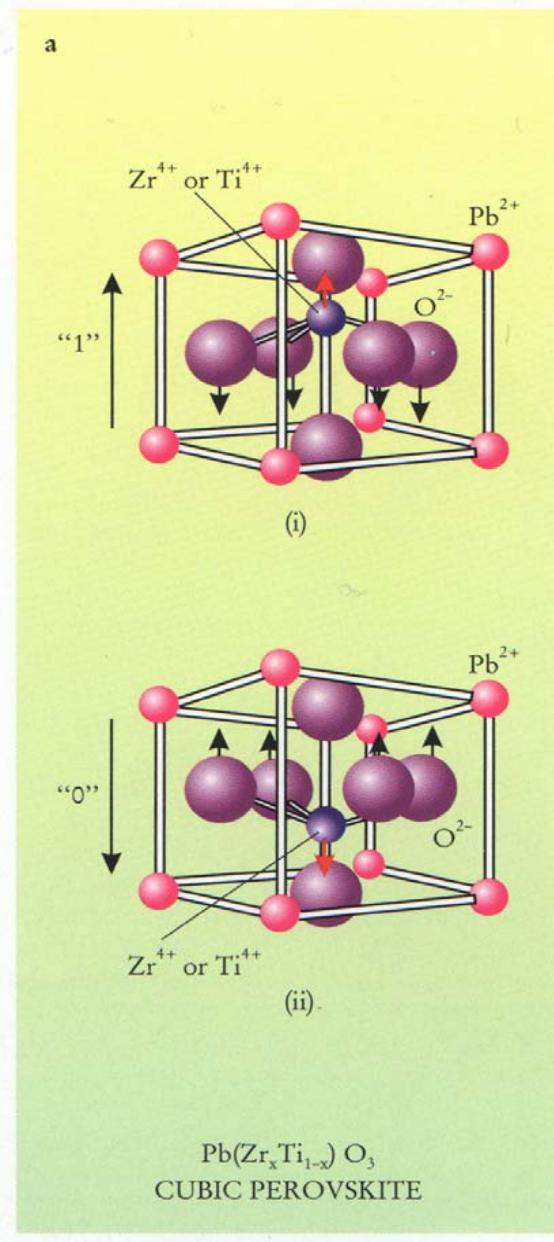
**R.Ramesh**

Department of Materials Science and Engineering and Department of Physics  
University of California, Berkeley

# Outline

- # **Introduction and Motivation**
- # **The World Of Crystalline Oxides on Semiconductors**
- # **Specific Examples**
  - Ferroelectric Oxides
  - CMR Oxides ; DMS Oxides
  - Self-assembled magnetic nanostructures
  - Multiferroic Oxides and Nanostructures
- # **Summary : Challenges and Opportunities**

# Complex Oxides : Crystal Structure



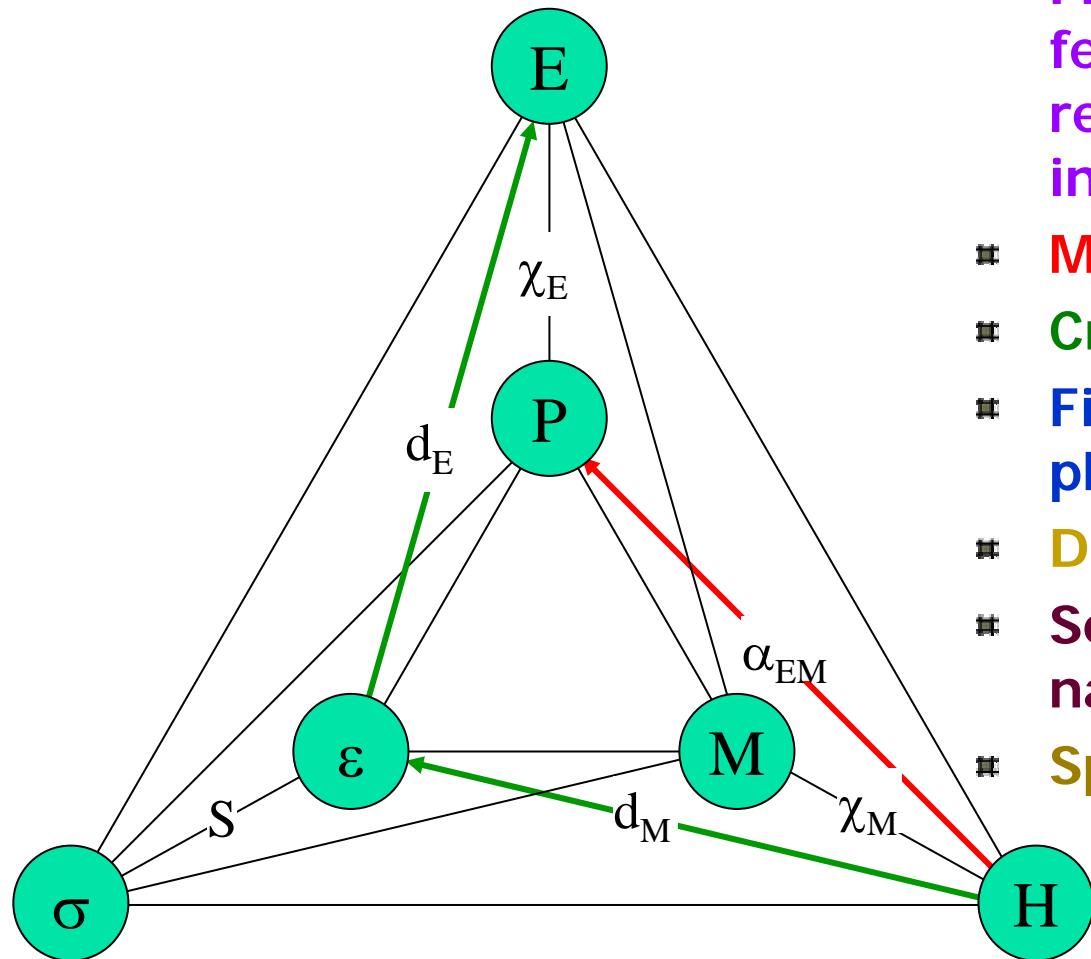
# Functional Oxides

- High  $\epsilon_r$  Insulators ( $\text{SrTiO}_3$ )       $\rho \approx 1 \times 10^{13} \Omega\cdot\text{cm}$   
 $\epsilon_r = 20,000$  (4 K)
- Low  $\epsilon_r$  Insulators ( $\text{LaAlO}_3$ )       $\epsilon_r = 25$  (300 K)
- Conductors ( $\text{Sr}_2\text{RuO}_4$ )  $\rho_{a,b} \approx 1 \times 10^{-5} \Omega\cdot\text{cm}$  (77 K)
- Superconductors ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ )       $\rho \approx 0$
- Ferroelectrics ( $\text{PbTiO}_3$ )       $P_r = 80 \mu\text{C}/\text{cm}^2$
- Semiconductors  
(doped  $\text{SrTiO}_3$ )       $\mu = 22,000 \text{ cm}^2/\text{V}\cdot\text{s}$  (2 K)
- Ferrimagnets ( $\text{PrFeO}_3$ )       $M_s = 0.04 \mu_B$
- Ferromagnets ( $\text{SrRuO}_3$ )       $M_s = 1.4 \mu_B$
- Antiferromagnets ( $\text{PrNiO}_3$ )
- Colossal Magnetoresistance (( $\text{La},\text{Sr})\text{MnO}_3$ )  
 $\Delta R/R_H > 10^4$  (6 T)
- High Thermal Conductivity ( $\text{LaCoO}_3$ )
- Catalysts ( $\text{La}(\text{Ti},\text{Cu})\text{O}_3$ )

All Perovskite-Related with  $a,b \approx 3.8\text{-}3.9 \text{ \AA}$

# Areas of Research

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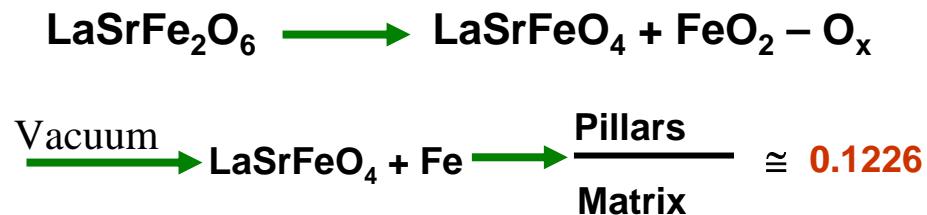
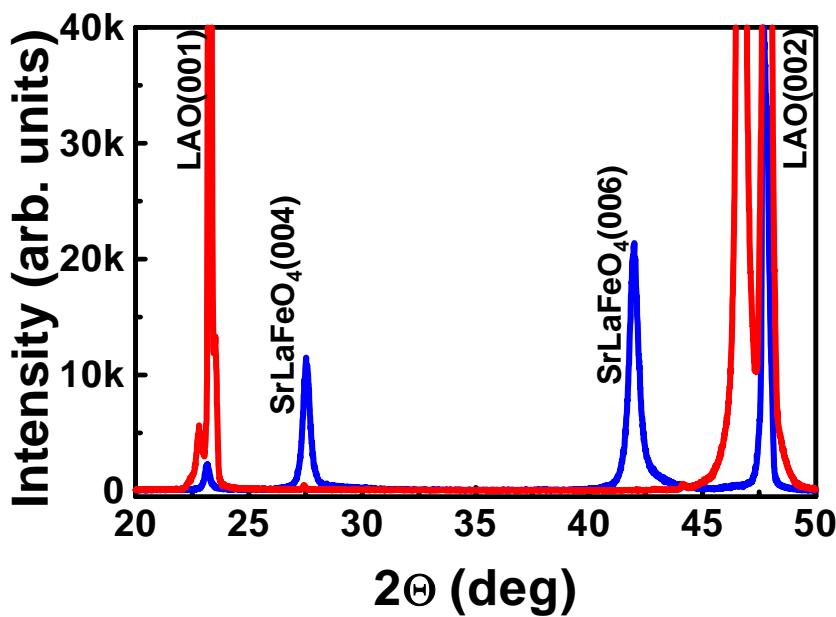
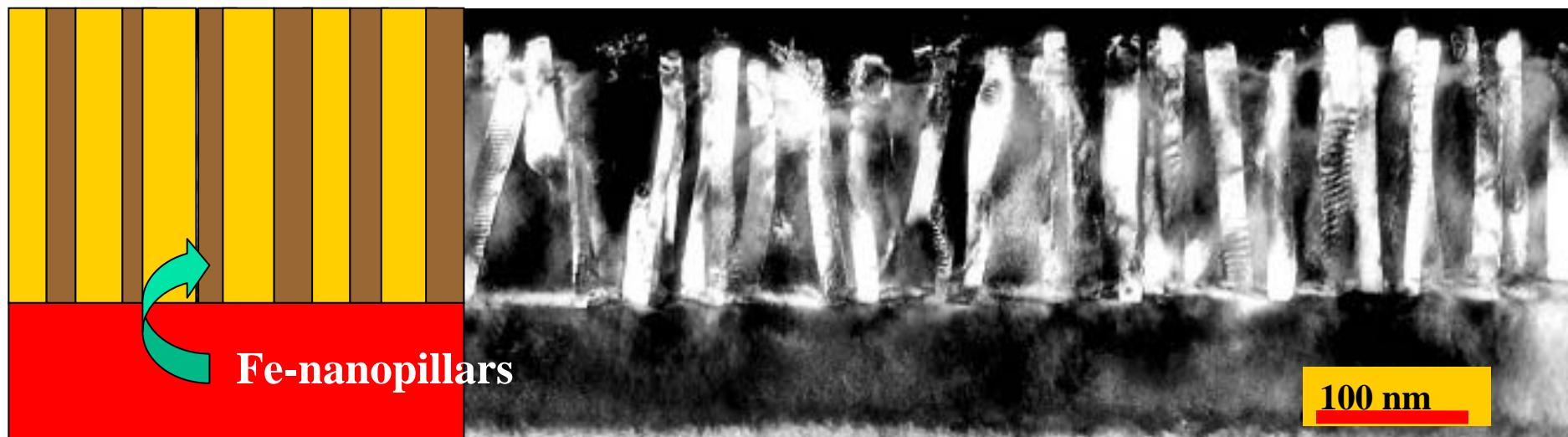
- # **FERAM's ; Domain dynamics in ferroelectrics: switching and relaxation ; finite size effects ; integration on Si ; reliability**
- # **Multiferroic Oxides : $\text{BiFeO}_3$  on Si**
- # **Crystalline Oxides on Si**
- # **Field effects and electronic phase separation in CMR/Si**
- # **Doped Insulators : Oxide DMS**
- # **Self-assembled magnetic oxide nanostructures**
- # **Spin-polarized Intermetallics**

# **Summary of Research Facilities**

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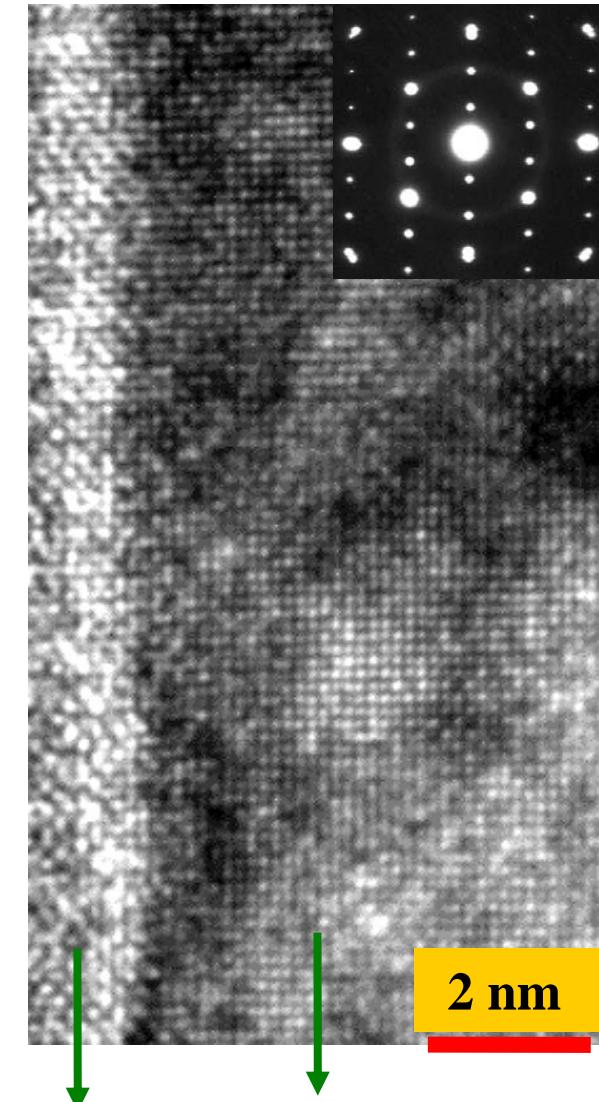
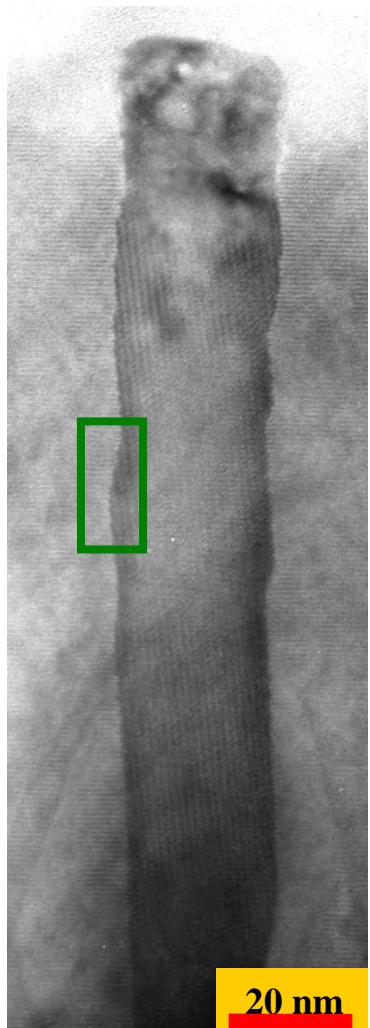
- # **Thin film processing : PLD, CVD, Sputtering, solgel**
- # **Laser MBE of complex oxides ; Crystalline Oxides on Si**
- # **Device processing in a dedicated clean room**
- # **Scanning force microscopy : Piezoforce microscopy of FERAMS ; nanoscale domain dynamics using AFM ; MFM ; TUNA ;**
- # **Switching dynamics using AFM ; high speed measurements**
- # **FE, transport, interface, pyroelectric studies**
- # **Insitu studies using synchrotron : Advanced Light Source**
- # **TEM studies : NCEM**

# Nanostructures through Spontaneous Phase Decomposition : Formation of Fe nanowires

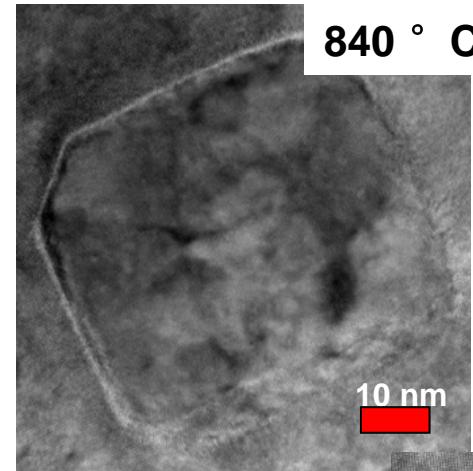


Experimental data:  $\approx 13\%$

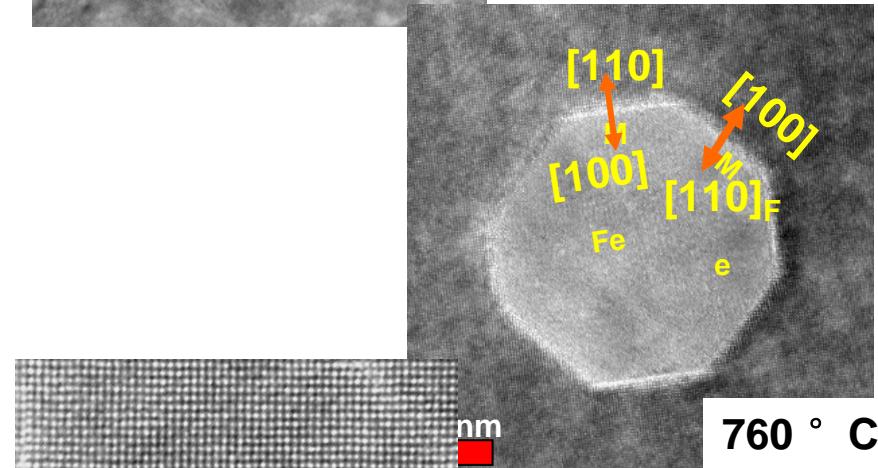
# Epitaxial Fe nanowires



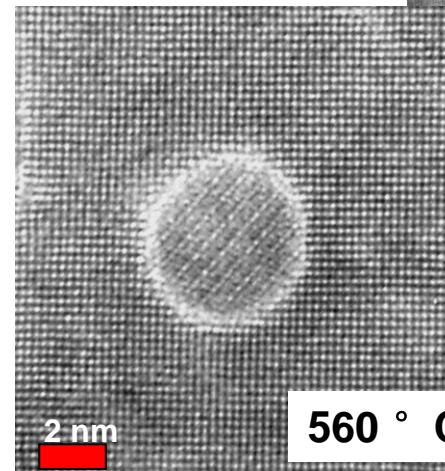
LaSrFeO<sub>4</sub>   Fe nanowires



840 ° C

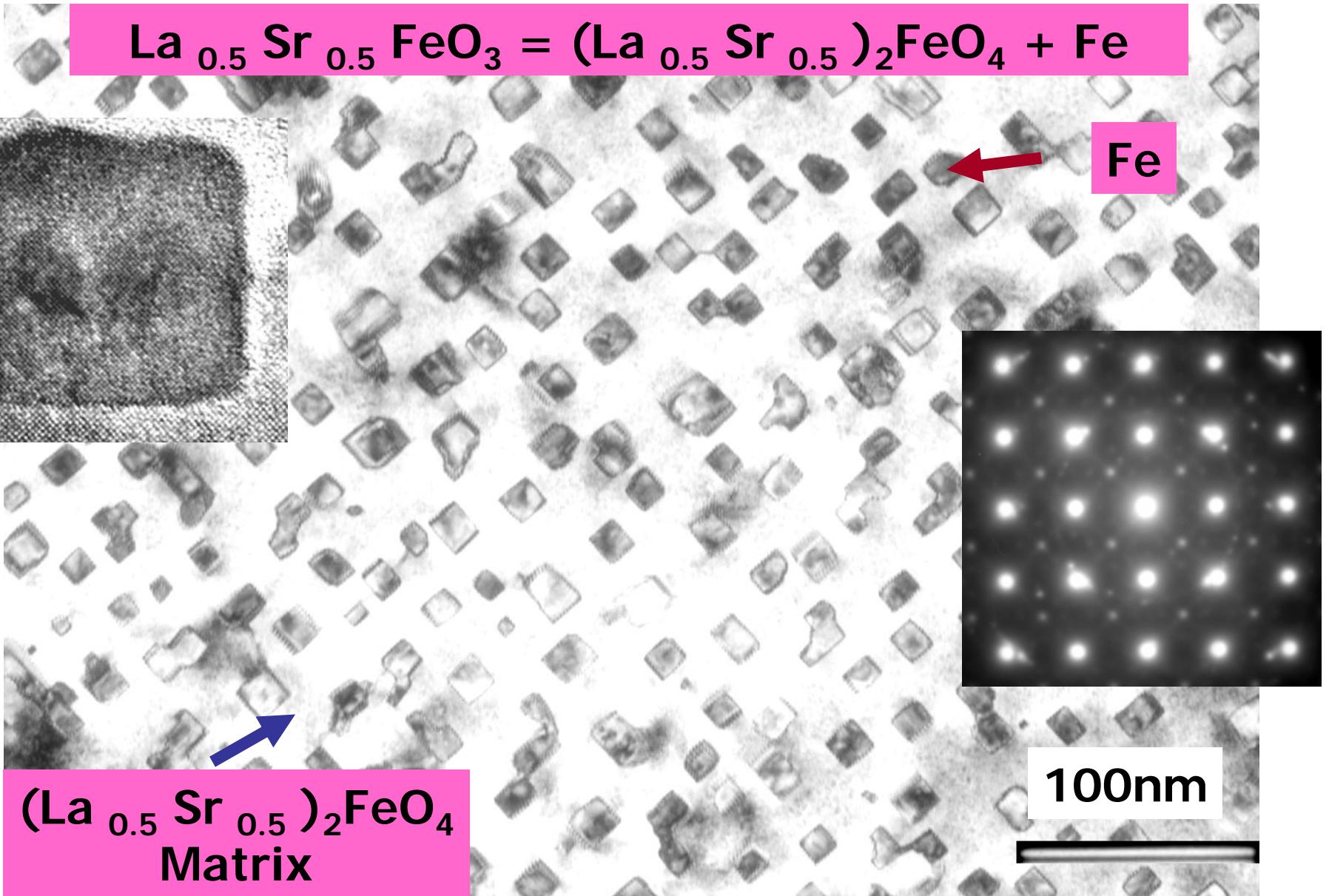


760 ° C

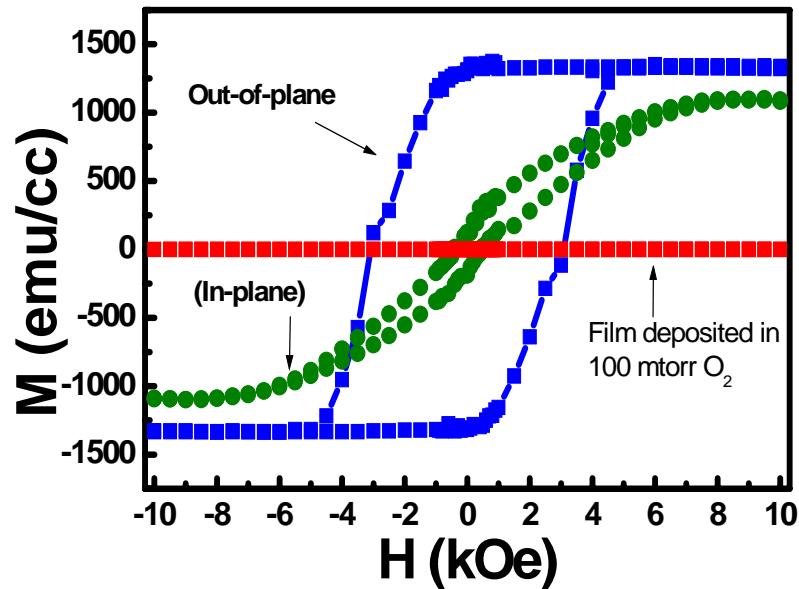
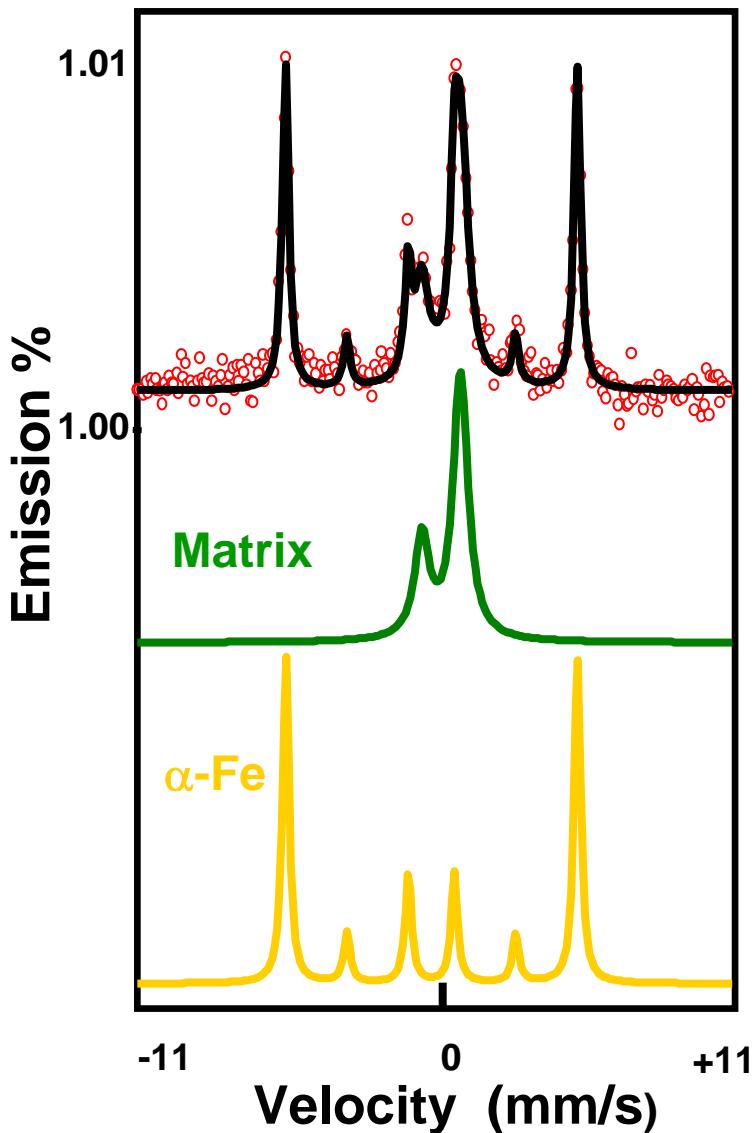


560 ° C

# Epitaxial Fe nanowires : Long range order ?



# Magnetic Properties of Fe-nanopillars

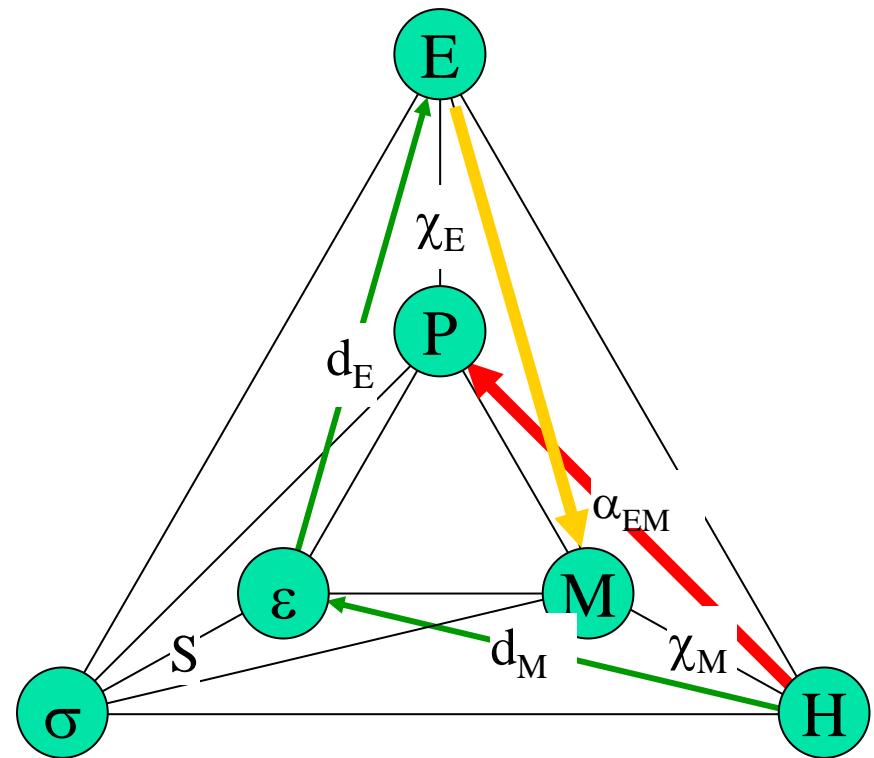


Vacuum deposited films : Strong ferromagnetism  
Films deposited in Oxygen : Antiferromagnetic

Mossbauer : shows coexistence of  
Ferromagnetic Fe and paramagnetic matrix

Control of order among nanowires  
Magnetotransport is critical

# Multifunctional Complex Oxide Heterostructures



Magnetism  
Magnetostriiction  
Magneto optics  
Magnetotransport

Ferroelectricity  
Piezoelectricity  
Electrooptics

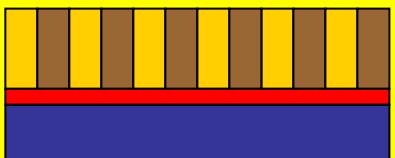
Coupling of order parameters  
Large cross-susceptibilities



Single Phase



Heterostructures/  
Superlattices

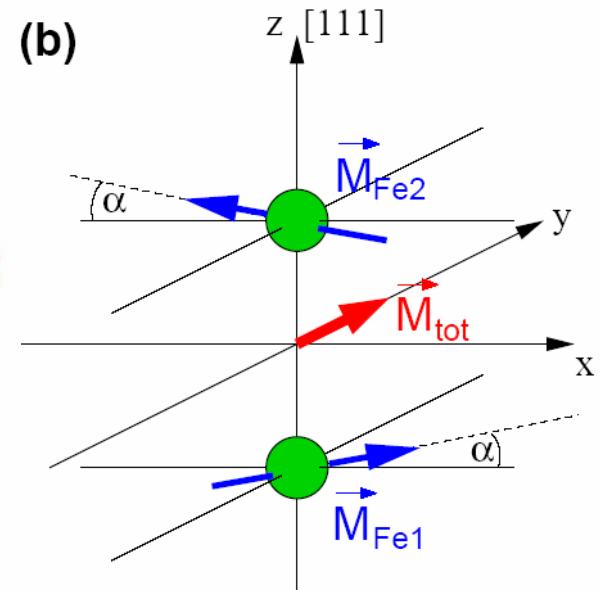
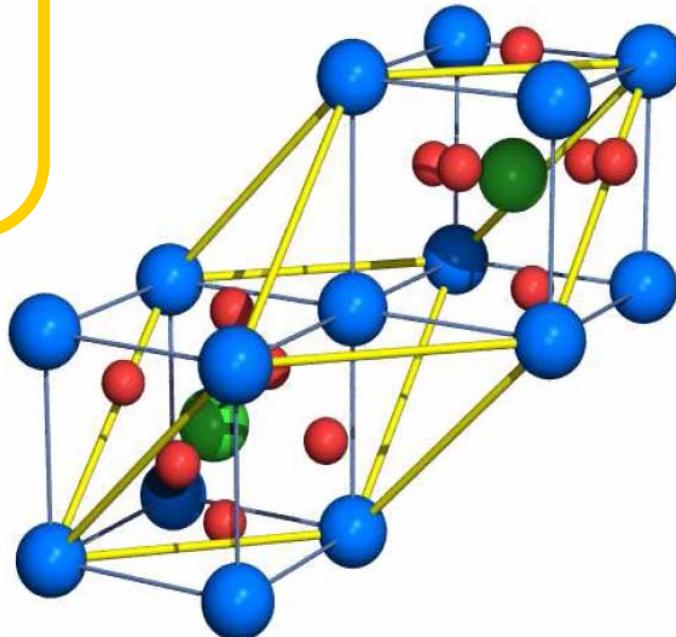


Vertical  
heterostructures

Energy Conversion/  
Transduction  
Field tunable Photonic  
Bandgap Structures  
Information Storage  
Radiation Sensing  
Energy Storage Systems

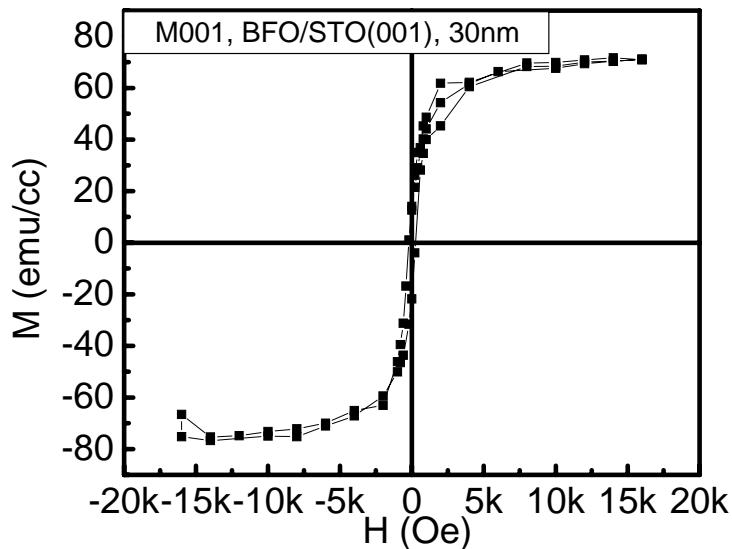
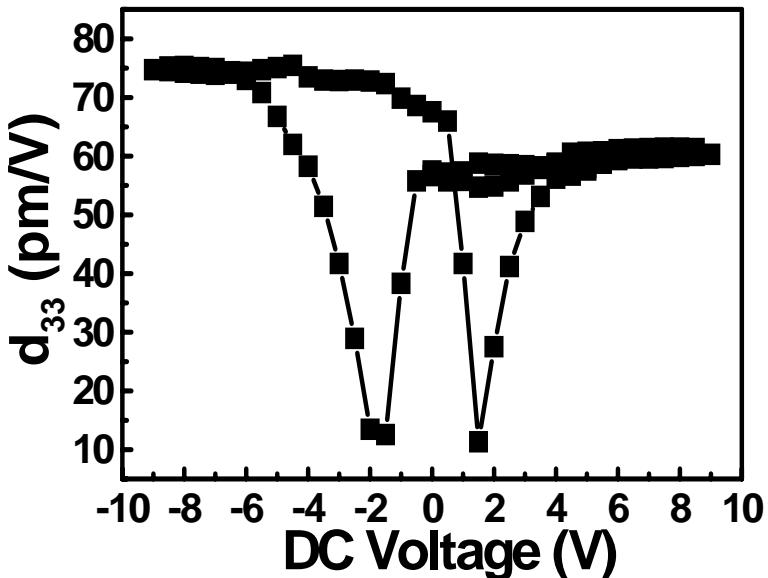
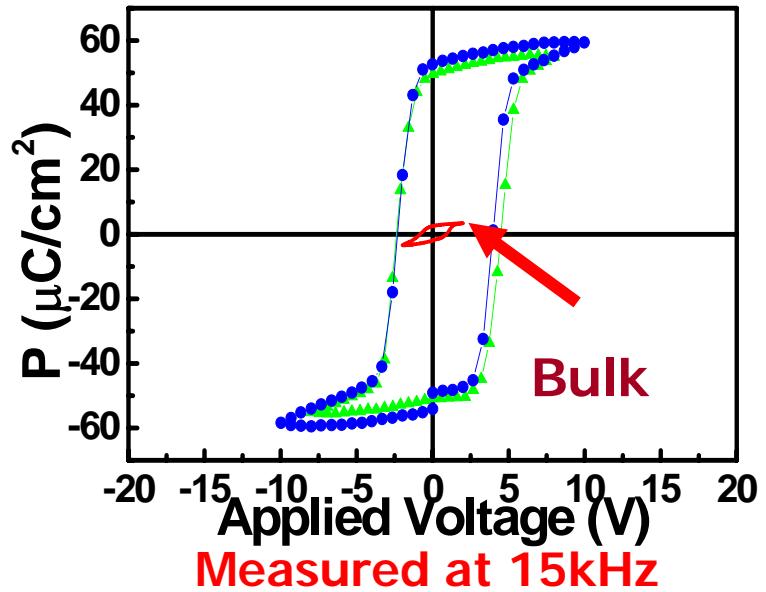
# Structure of Bulk BiFeO<sub>3</sub>

$a=3.965\text{\AA}$ ,  $\alpha = 89.46^\circ$   
 $T_N=643 \sim 673\text{K}$   
 $T_C=1118 \sim 1123\text{K}$   
 $P_s=3.5\mu\text{C}/\text{cm}^2$   
(100)??



- Rhombohedral, R3c
- Rotation of octahedra about [111] ; displacement of Fe
- Canted, spiral G-type, AFM order : no effective moment in low field
- Small magnetization in bulk : 8-10 emu/cc in a field of ~180T
- Ferroelectricity in bulk : unusually low P ??

# Magnetism and Ferroelectricity Epitaxial / BiFeO<sub>3</sub> / SrRuO<sub>3</sub> on STO and STO/Si



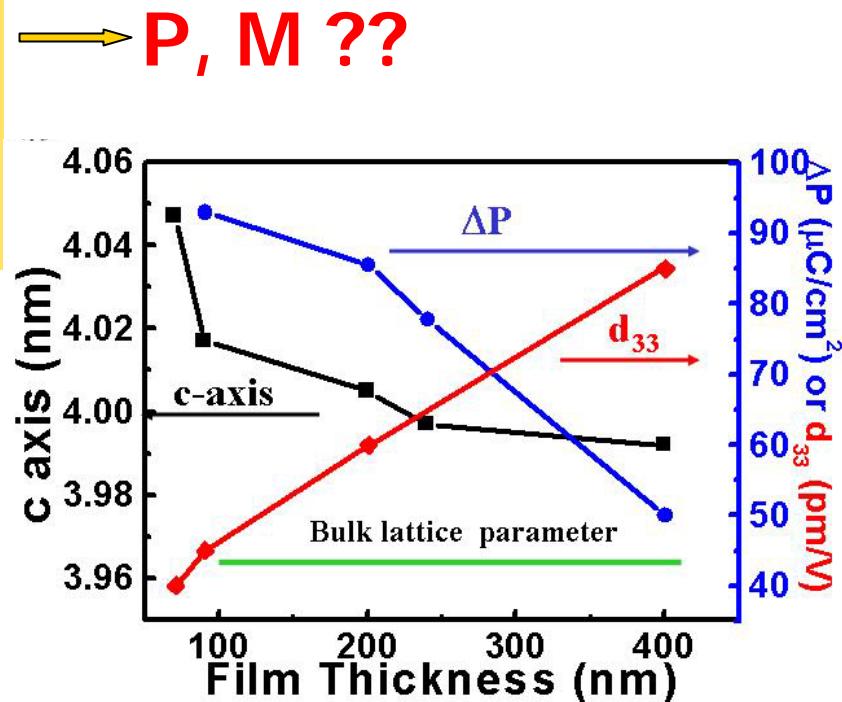
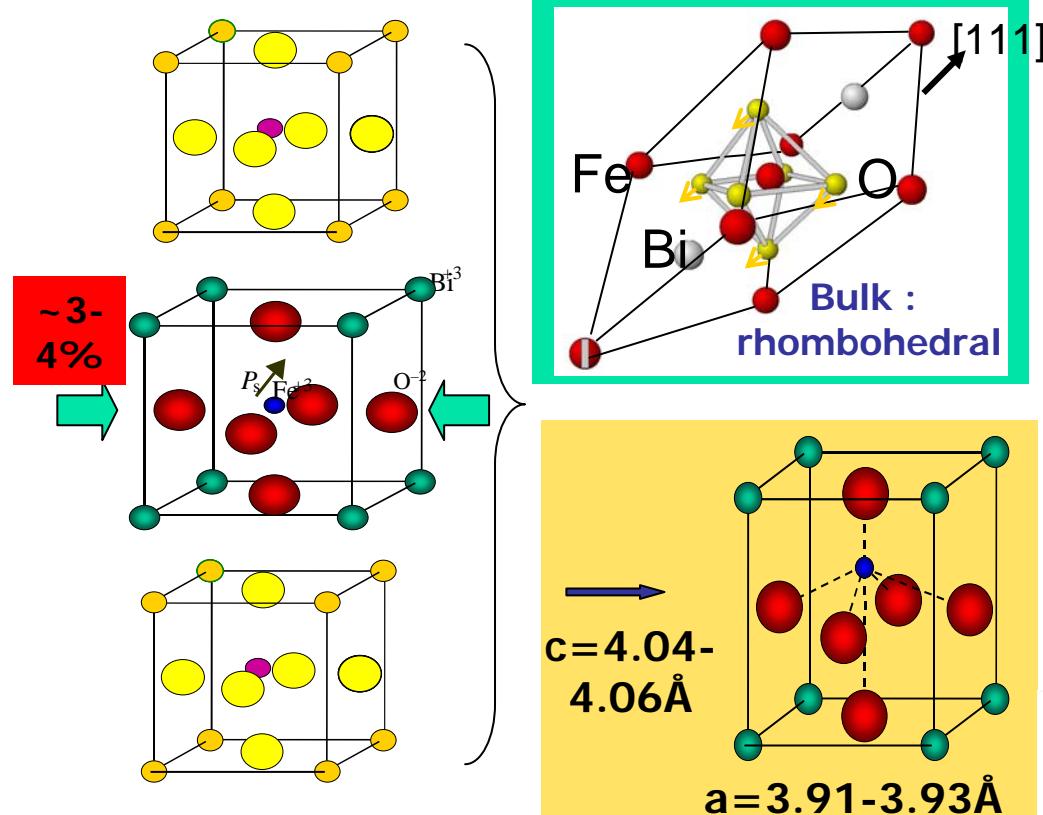
Bulk : G-type antiferromagnet ; low  $P$ (maybe due to processing ??)

Thin Films : Large  $P$  ; measurable magnetic moment

Origin of Magnetism ?

Coupling of order parameters  
(PFM/MFM ; Optics, microwave)

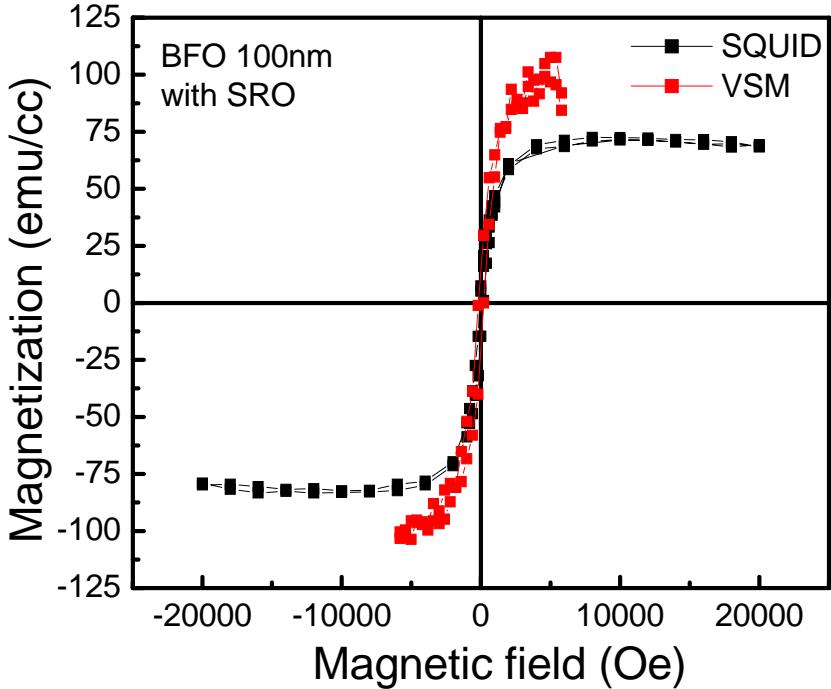
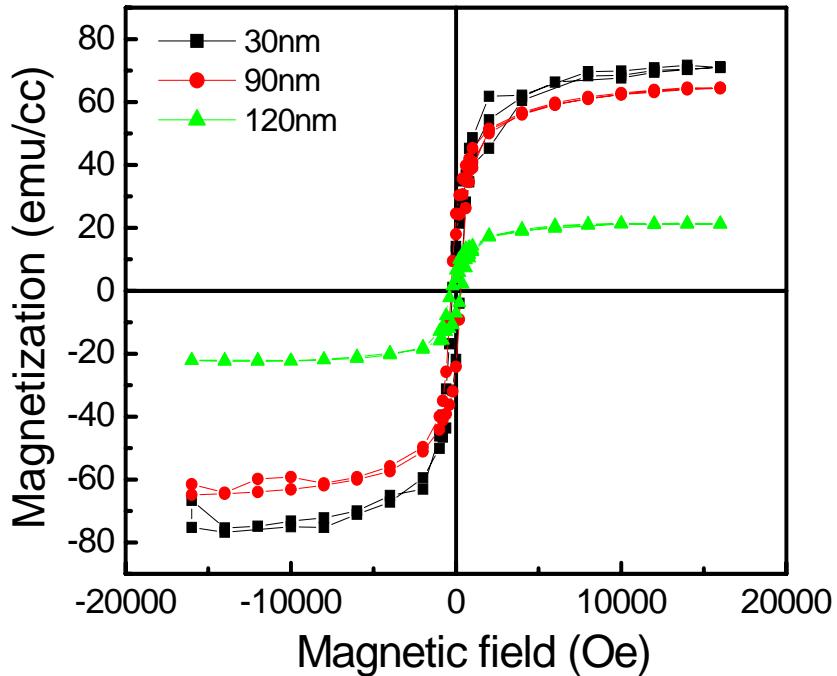
# Heteroepitaxial $\text{BiFeO}_3$ on (100) STO



On (100) STO :

- tetragonal distortion + rhombohedral structure = monoclinic symmetry
- “monoclinicity” depends on film thickness

# Magnetic Properties of Thin Film BiFeO<sub>3</sub> on (100) STO



X-ray analysis does not show any macro-size second phase

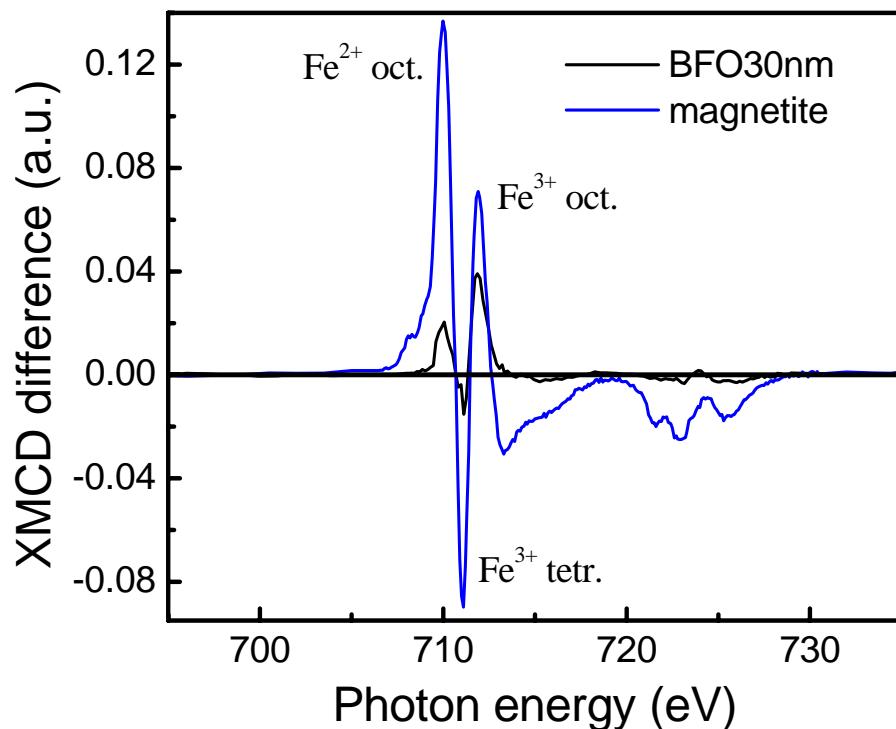
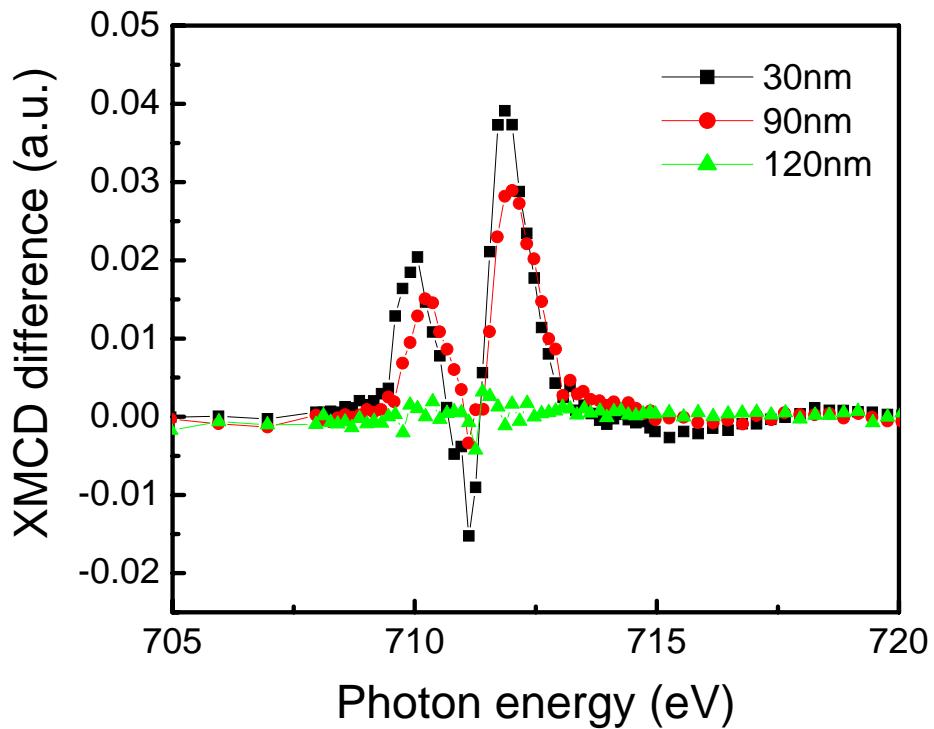
AFM, TEM : no second phase

RBS indicates Bi/Fe ratio ~1

Possible role of oxygen related defects ?

# Origin of Magnetism : Heteroepitaxy & Defect Chemistry

## Probing through XAS / XMCD



### Key Points

Existence of Fe<sup>+2</sup> (XPS, XMCD)

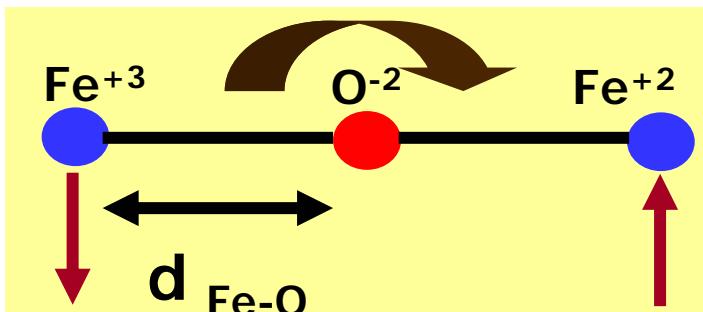
Moment is ~15% of Fe<sub>3</sub>O<sub>4</sub>

Site occupancy is different from Fe<sub>3</sub>O<sub>4</sub>

Fe+3 in tetrahedral site : Puzzling??

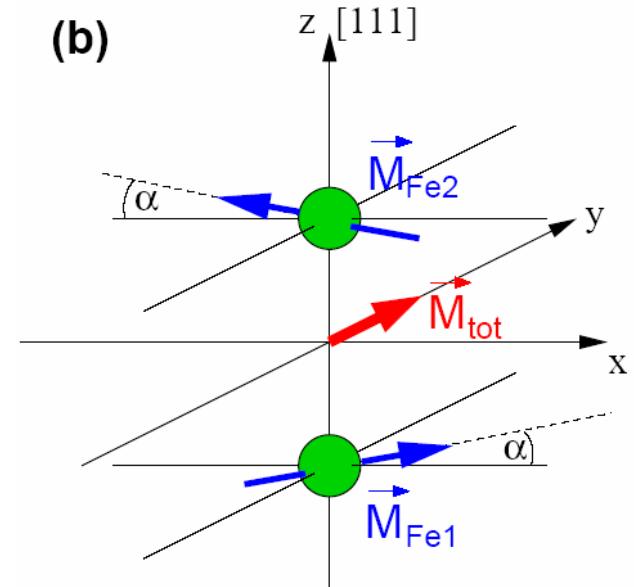
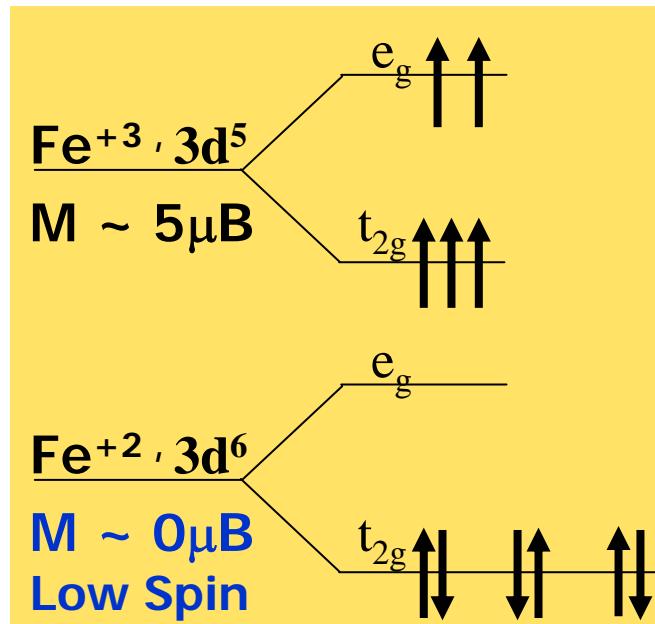
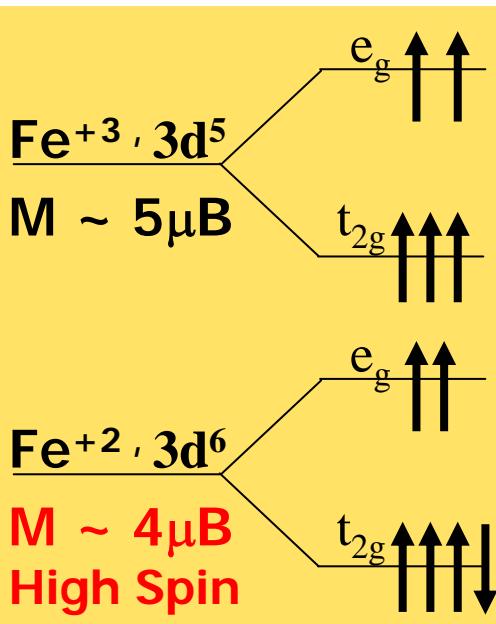
Need better understanding and modeling of MCD data

# Possible Origins of Magnetism

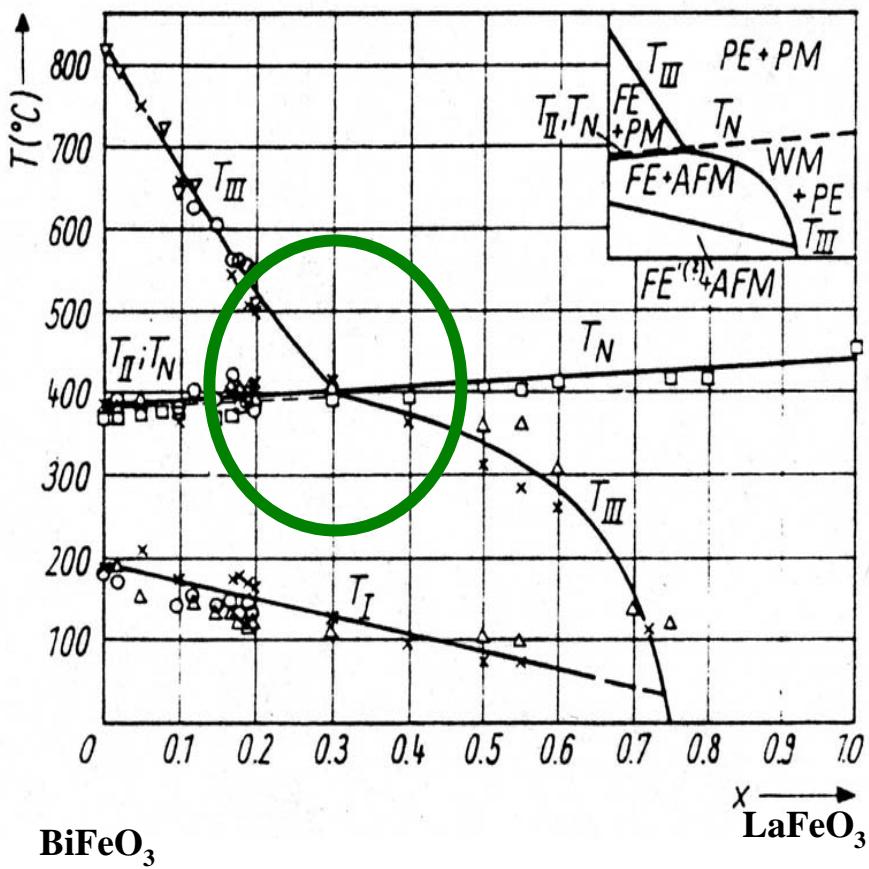


Antiferromagnetic  
Super-exchange

- Need to understand Fe-O defect chemistry under heteroepitaxial constraints
- Electronic structure of  $\text{Fe}^{+3}/\text{Fe}^{+2}$  under Heteroepitaxial stresses
  - Spin canting effects under combined oxygen defect-electronic structure effects



# Tuning Phase Transitions



## FUTURE DIRECTIONS

Magnetism in BFO:  $\text{Fe}^{+2}/\text{Fe}^{+3}$

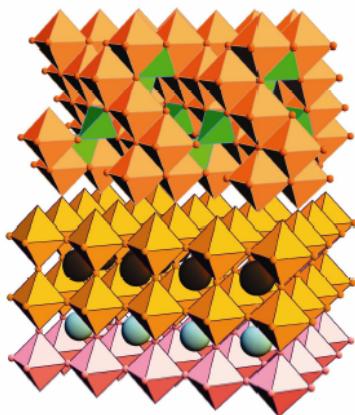
$(\text{Bi, RE})(\text{Fe,Cr})\text{O}_3$  : enhance magnetism

$\text{LaBiFeO}$  : enhance coupling thru phase transitions

Need interplay between experiment and theory : KEY

# Perovskite-Spinel Multifunctional Heterostructures

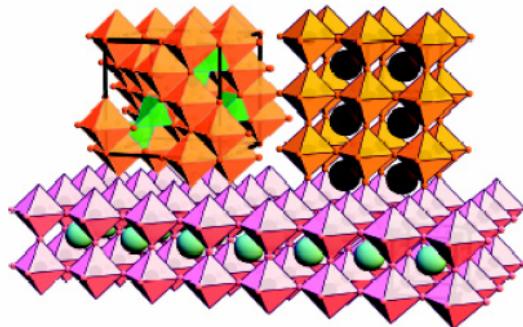
A



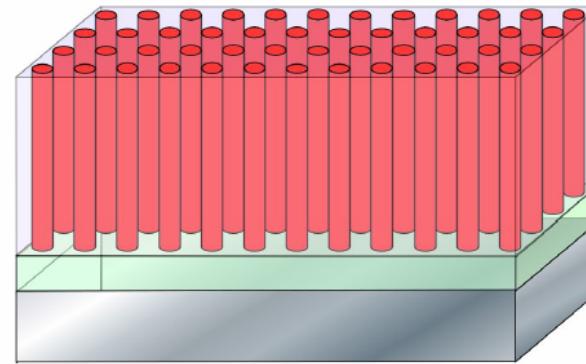
B



C



D



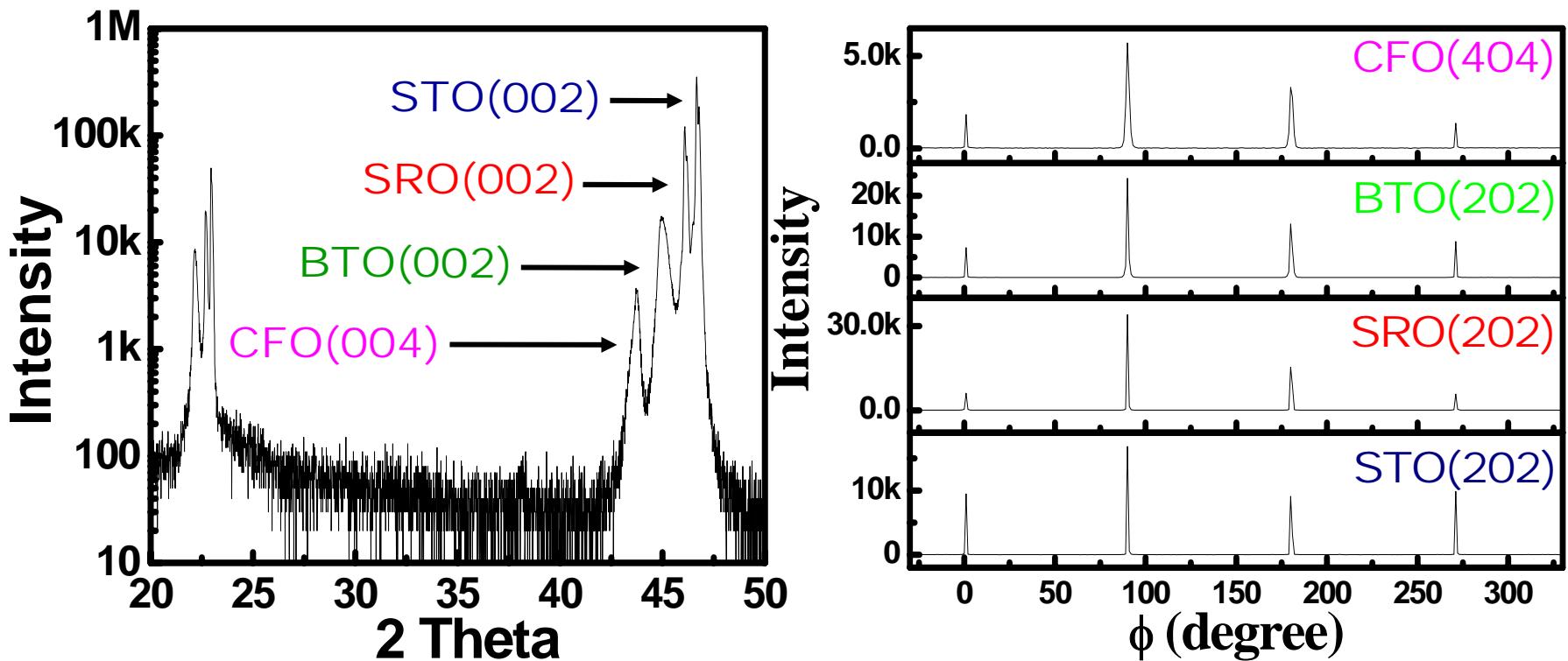
Spinel ( $\text{CoFe}_2\text{O}_4$ )  
 $a \sim 8\text{\AA}$

Ferrimagnet with  
Large Magnetostriction

Perovskite  $\text{BaTiO}_3$   
 $a \sim 4\text{\AA}$   
Ferroelectric / Piezoelectric  
Landau Parameters known

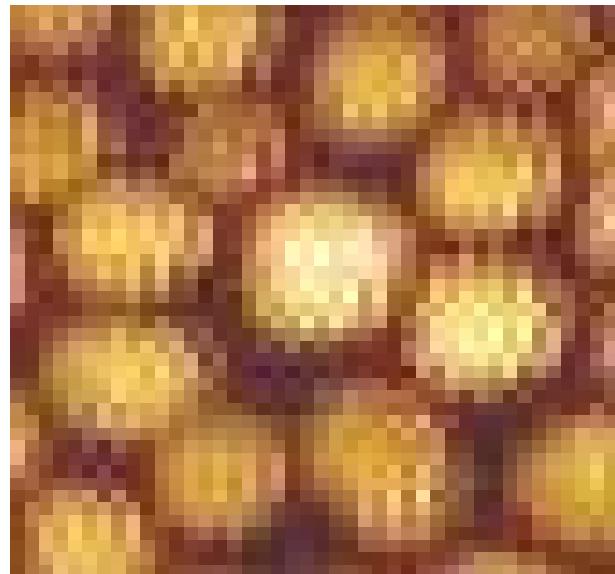
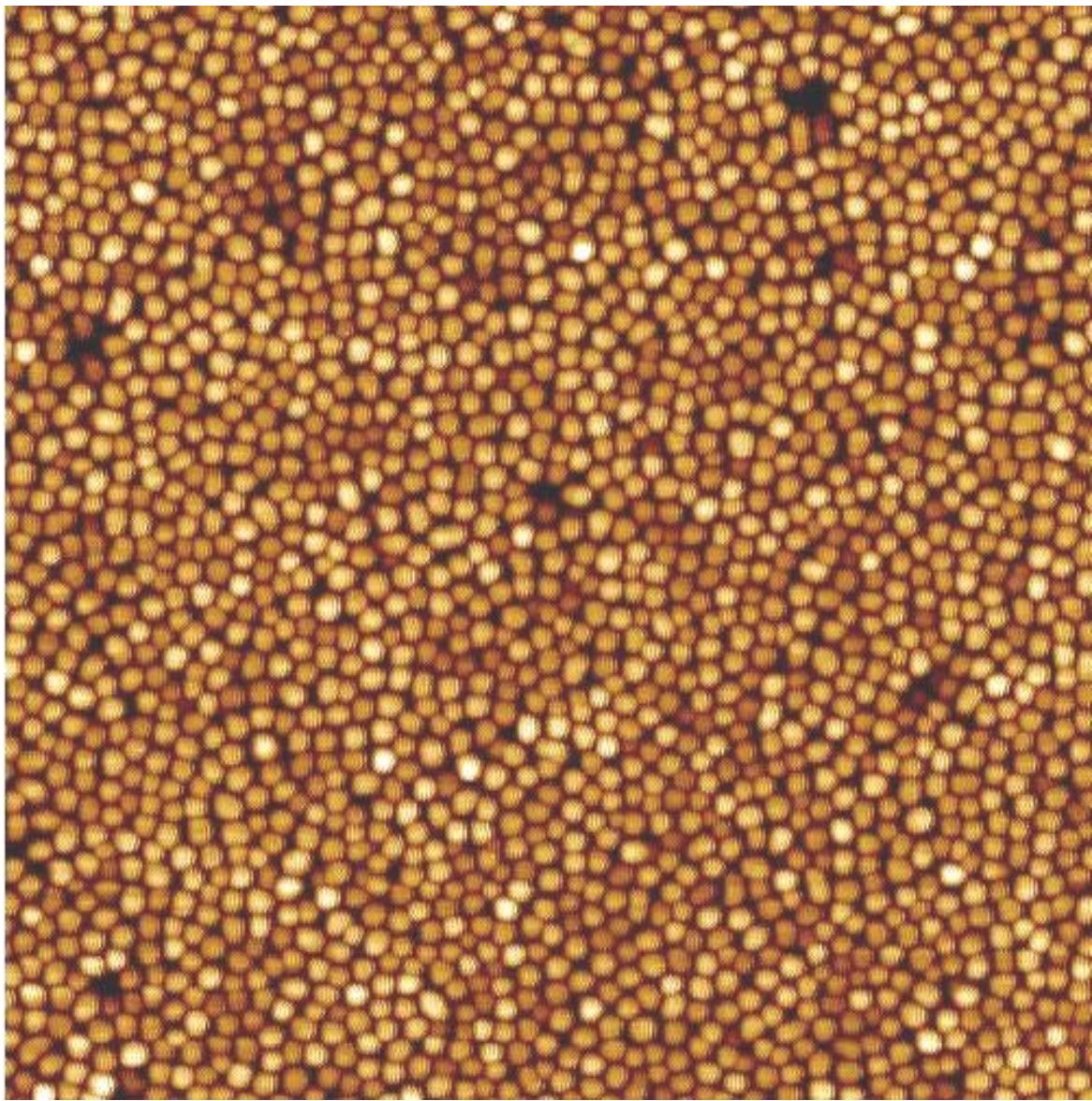
Coherent interface :  
enhance coupling  
Elastic Interactions :  
ordered structures

# Self-assembled $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ Nanostructures

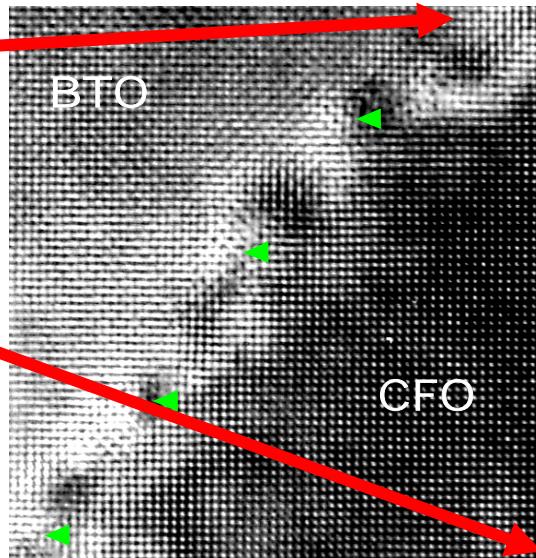
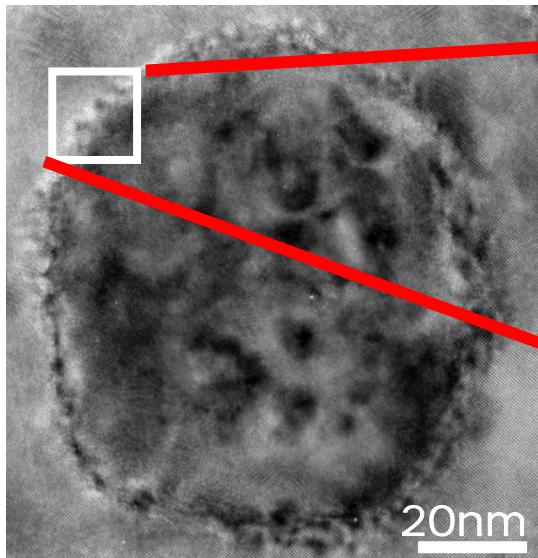
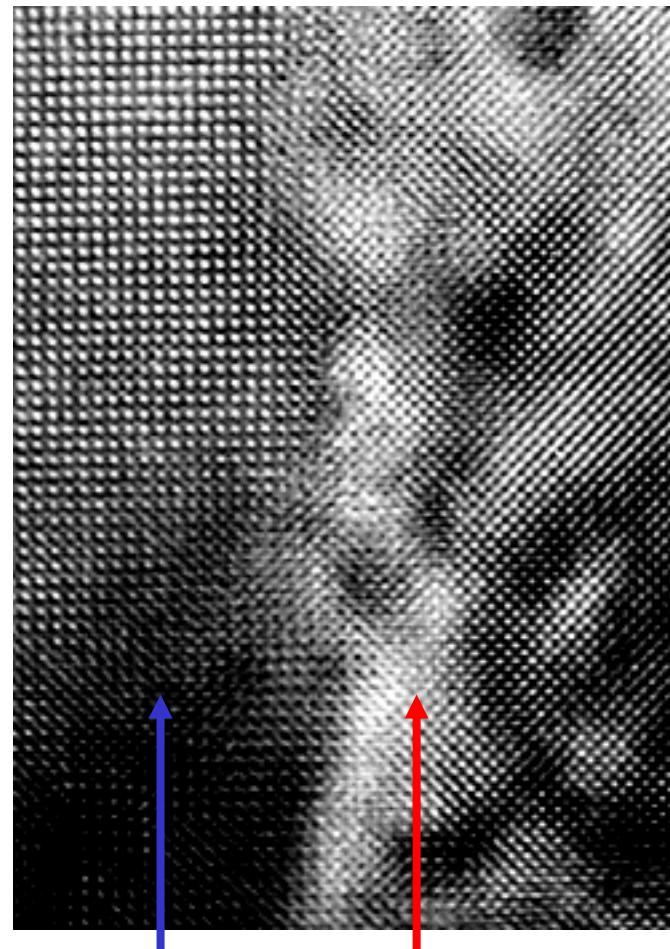
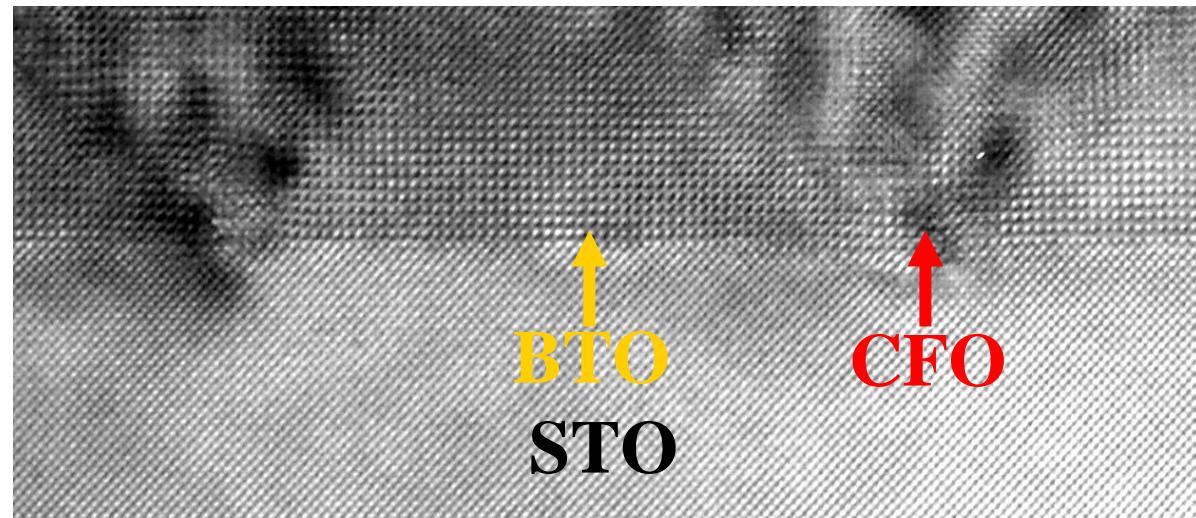


- XRD studies show phase separation of CFO and BTO
- Both phases are heteroepitaxial.

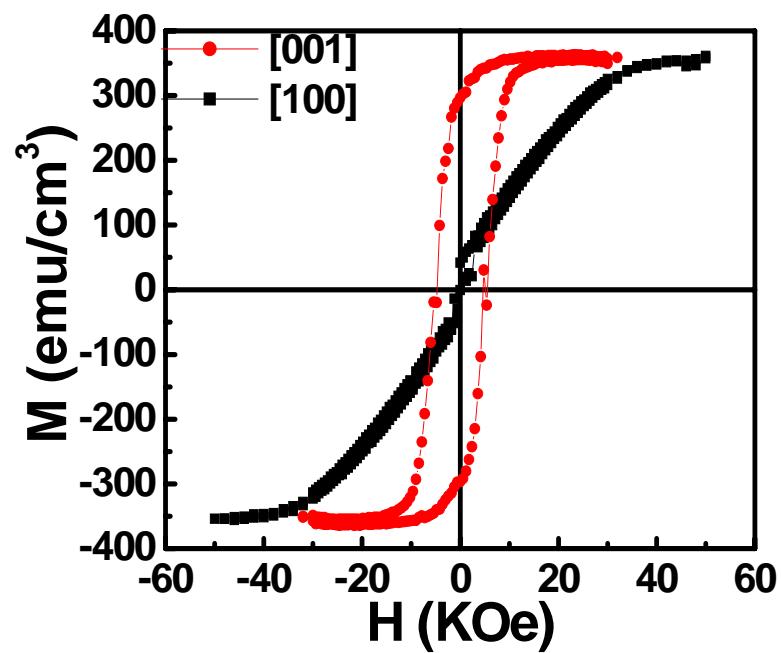
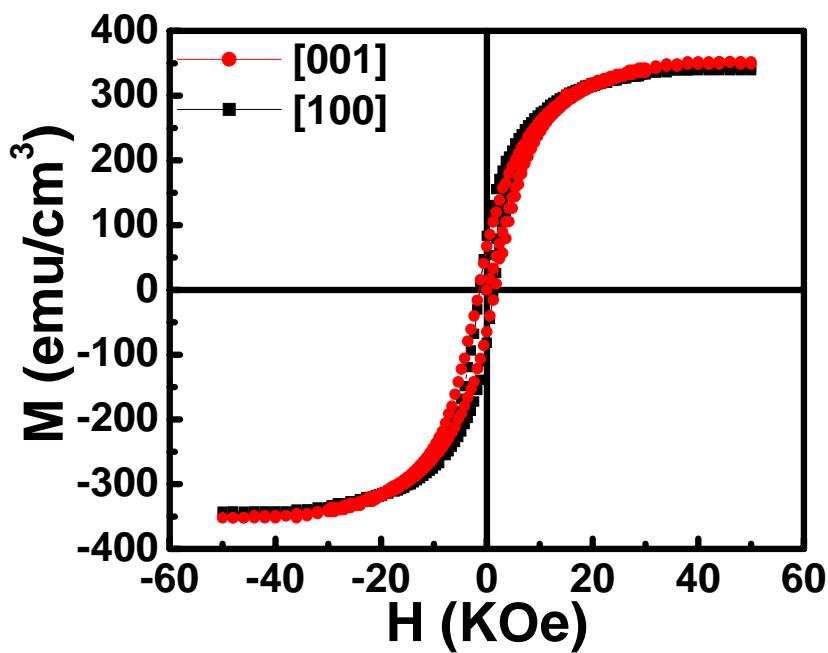
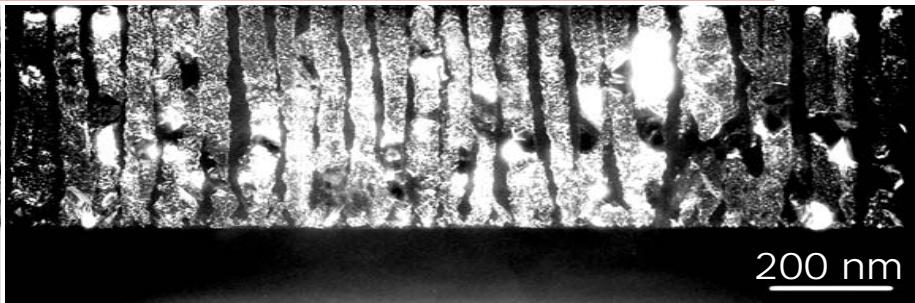
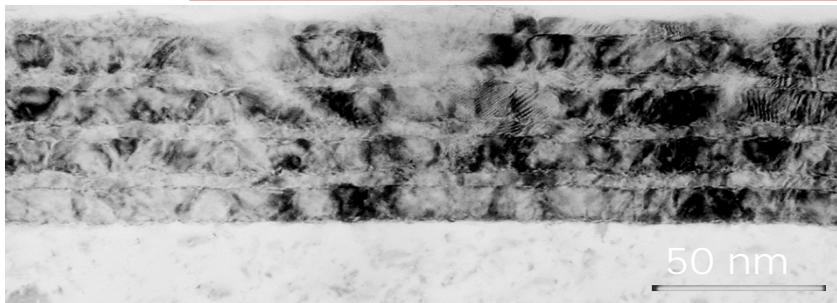
# Vertically aligned $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ heterostructures



# 3-D Heteroepitaxy



# Magnetic Properties



Anisotropy Field: ~35 KOe

Bulk CFO  $M_s$  350 ~ 400 emu/cm $^3$

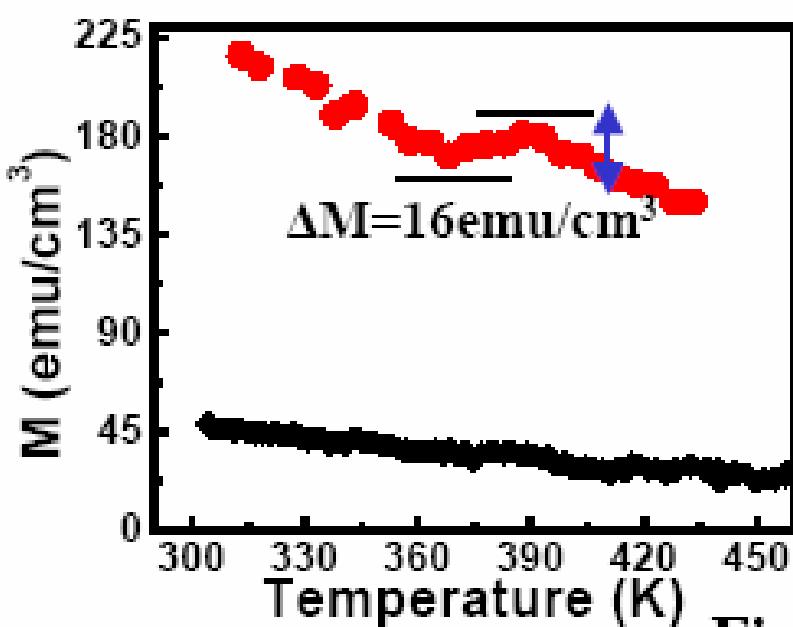
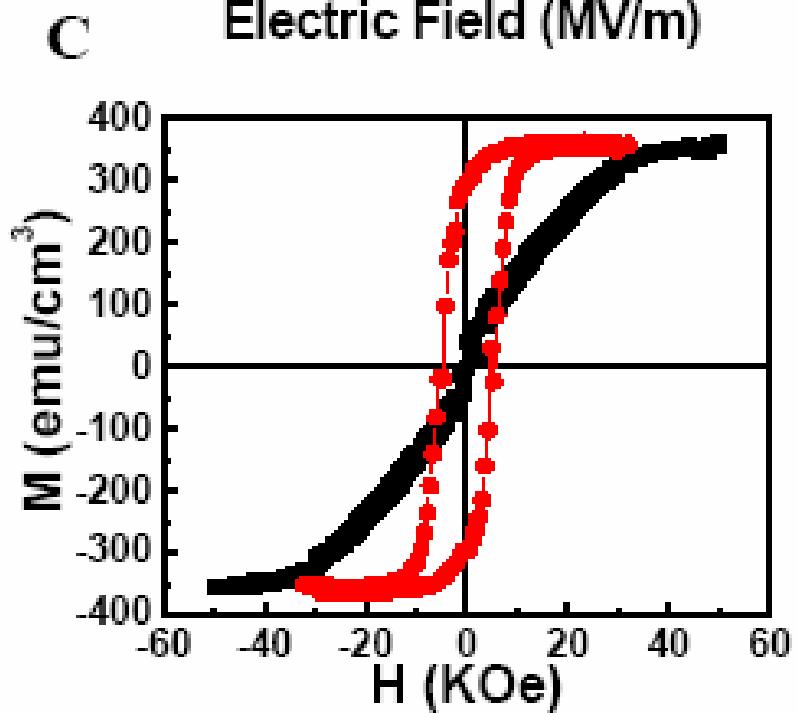
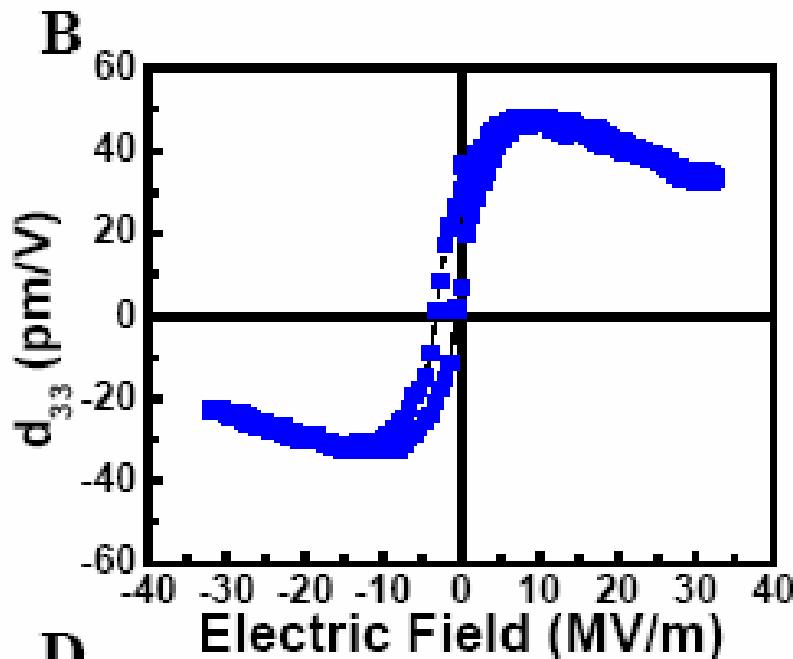
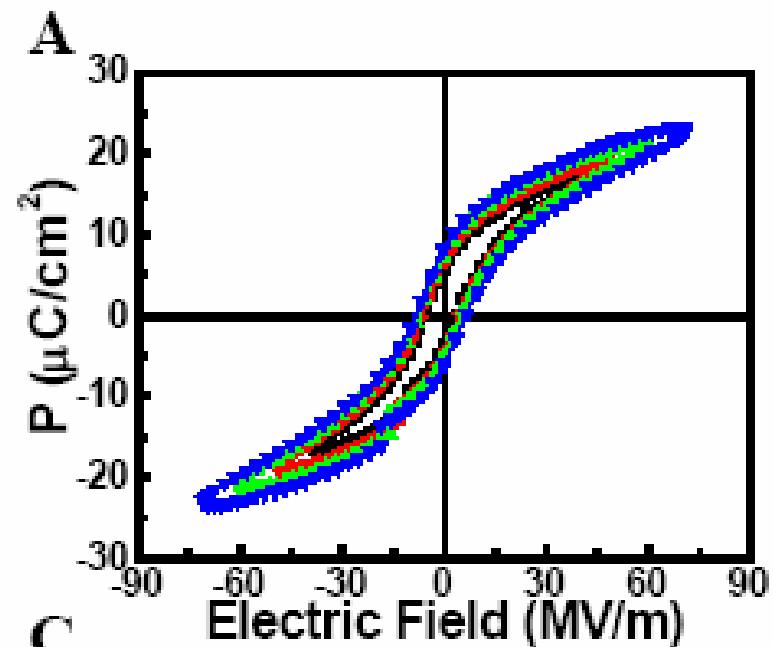
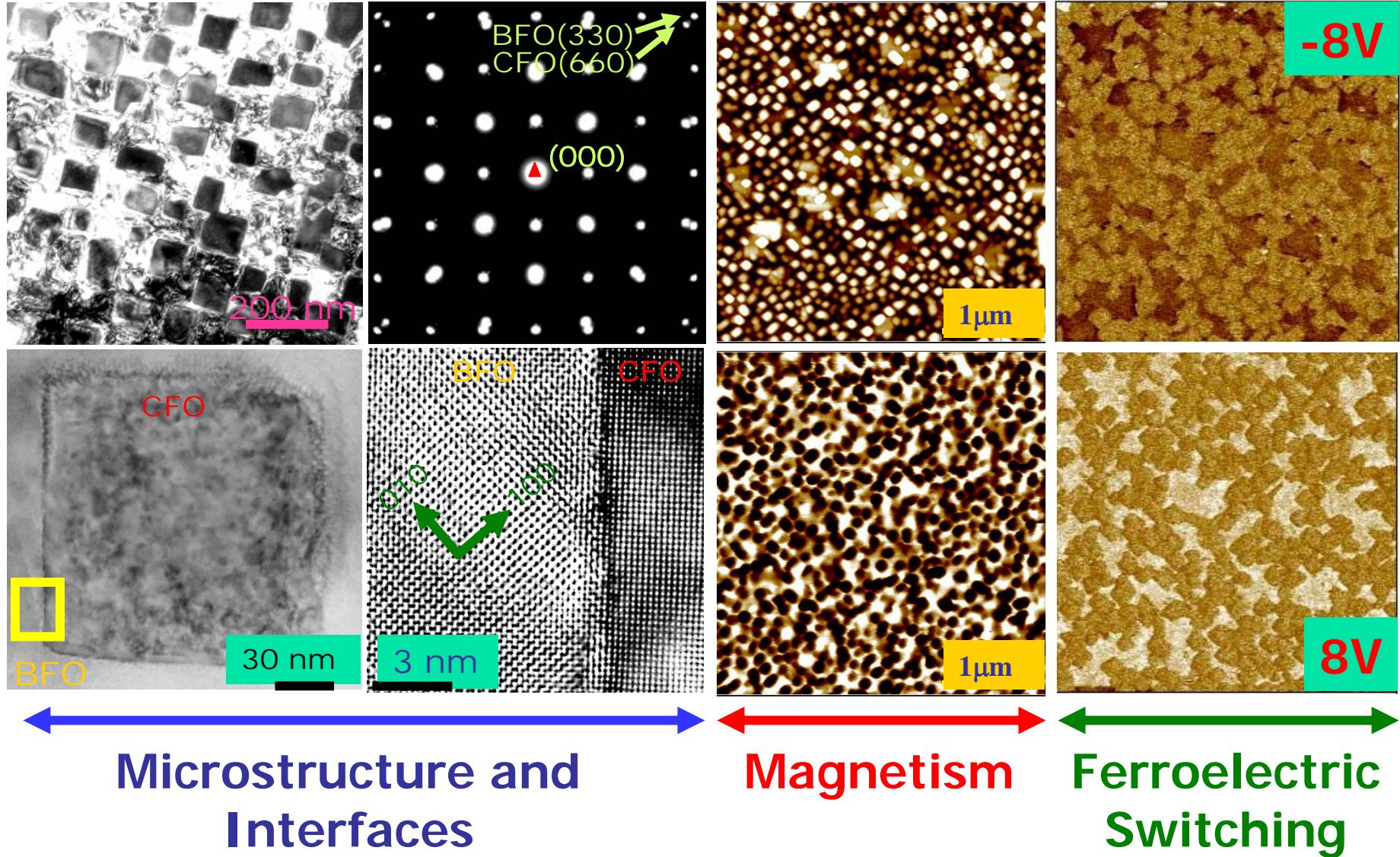


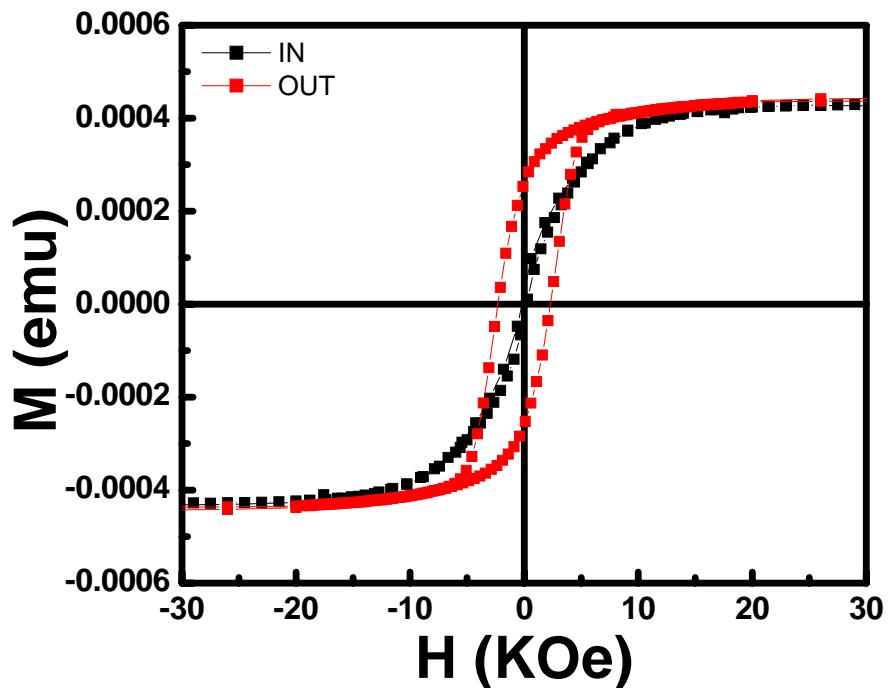
Fig.3

# $\text{BiFeO}_3/\text{CoFe}_2\text{O}_4$ System

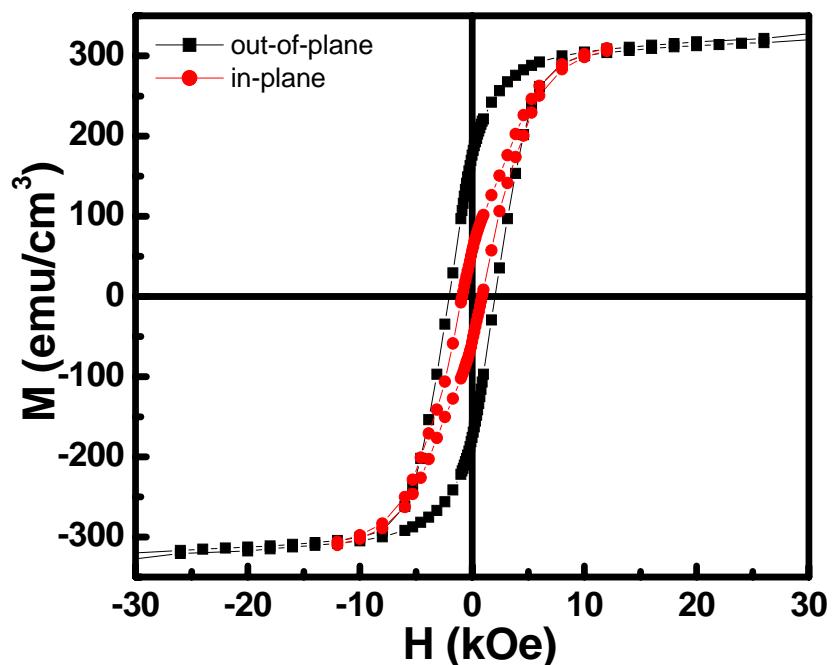


# Enhancements in Magnetic Anisotropy

$\text{BaTiO}_3 - \text{NiFe}_2\text{O}_4$

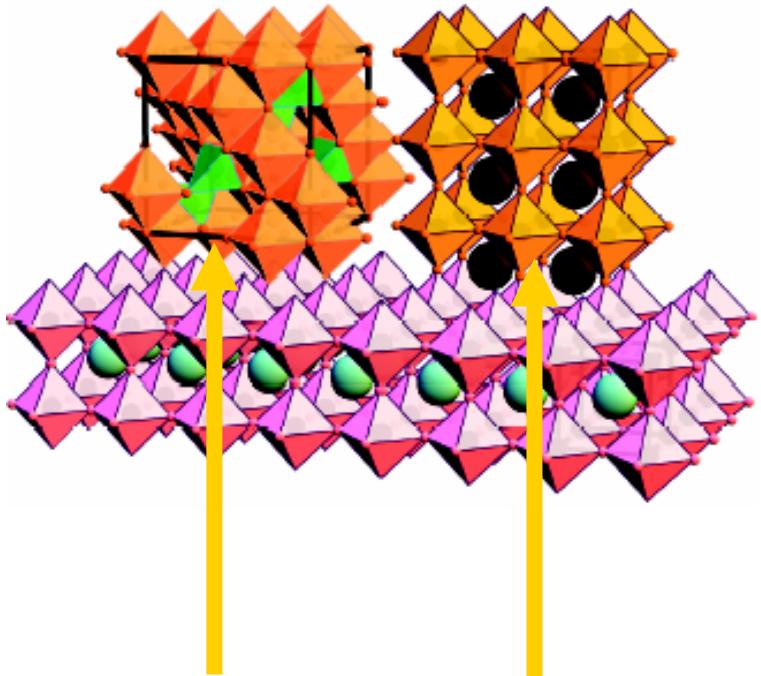


$\text{BiFeO}_3 - \text{CoFe}_2\text{O}_4$



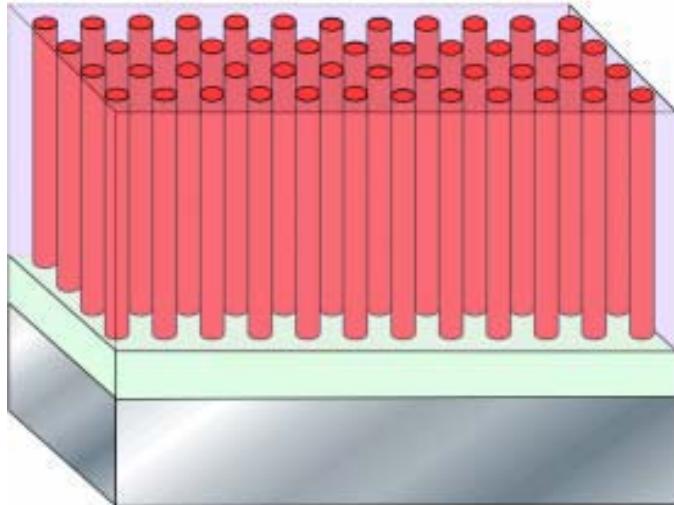
Enhancements in anisotropy seem generic to many systems  
Enhancements also depend on diameter of nanopillar

# Designing Multifunctional Nano-composites : A Generic Approach



**Phase A**  
Lattice Parameter :  $a$   
Line compound : no  
solubility of B in A

**Phase B**  
Lattice Parameter :  $n \times a$   
Line compound : no  
solubility of A in B

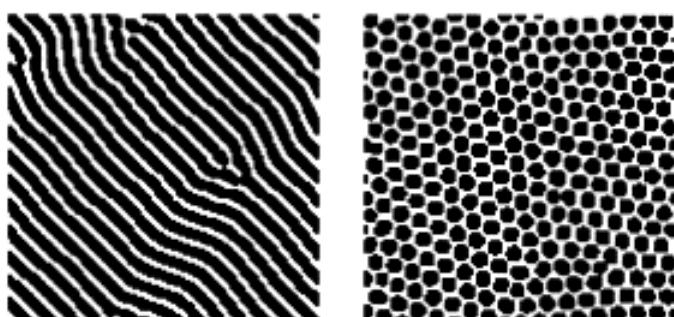
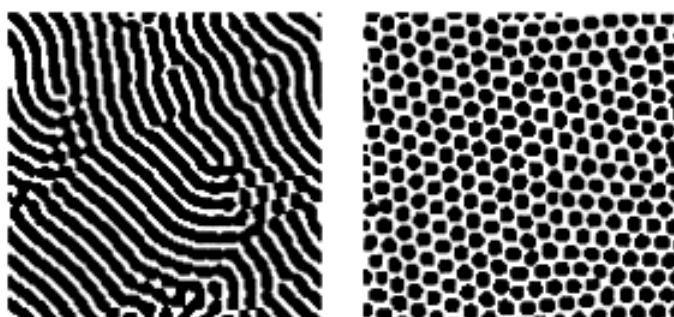


- **Coherent interface + Nano-scale : enhance coupling**
- **Self-assembly : ordered nanostructures ; control through heteroepitaxy**
- **Broad Impact**

# Challenges : Spontaneous Ordering in Nanostructures

## Taking a cue from semiconductors

Increasing lattice mismatch/ elastic constant difference



Increasing film thickness

Theoretically, it is possible to order the second phase!!

### KEY ISSUES

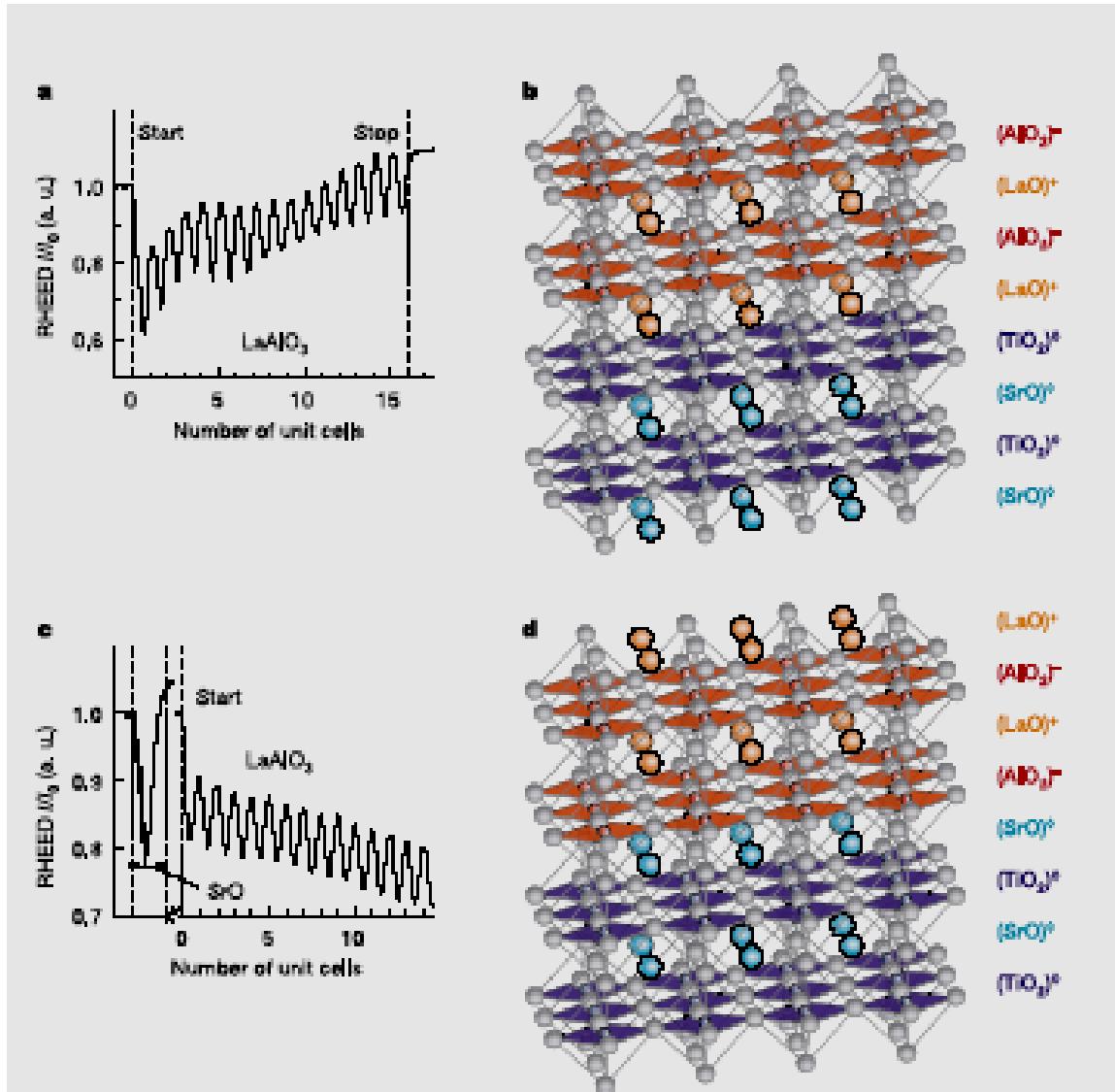
- Lattice mismatch effects  
(substrate/spinel/perovskite)
- Understanding growth mechanisms
- Crystal structure effects
- Need repulsive and attractive interactions

† Leonard and Desai, *Thin Solid Films* 357, p46  
(1999) ; Schuhkin and Bimberg, RMP, 1997.

## **Challenges : Coupling of Order Parameters**

1. Enhanced magnetic moments through Ferrimagnetism in Bi(RE)-Fe(Cr)-O<sub>3</sub>
2. Approaches to probe coupling : Optics ; microwave (e.g. resonance spectroscopy ; Proximal probes; synchrotron studies
3. Magnitude of coupling : Are the coupling coefficients large enough to be technologically valuable ?

# NEW DIRECTIONS : Tuned Heteroepitaxy



- Create New Properties at Interfaces in Complex Oxides
- Band vs. Mott Insulators
- Role of external perturbations and fields
- Possibility of 2-D e-gas ; possibly spin polarized

# Summary : Challenges and Opportunities

- **Functional Oxide Heterostructures** : An exciting area of basic and applied interdisciplinary research
- **Ferroelectric Memories** : products making their way into the market : interesting dynamics between **FRAM's** and **MRAM's** : capturing market share is the key !!
- **Scanned Probes** : Opening up new avenues for **spatially resolved** nanoscale probing of static and dynamic physical properties
- **Finite Size Effects** : PZT films clearly ferroelectric down to 4nm thickness ; suppression of ferroelectricity begins ~12 nm.
- **Theory / Experiment Coupling**: Very valuable!!
- Critical role for **in-situ** studies : growth studies on the **Synchrotron (ALS)**
- **BiFeO<sub>3</sub>** : lead-free ferroelectric / piezoelectric : very promising for memory / piezo / multifunctional applications
- **Multi-functional Oxide Heterostructures and Nanostructures** : Very exciting new developments ; great area of basic and applied interdisciplinary research
- **Self-assembly processes** : key to getting down to nano-dimensions : can we get nanopillars of FE in a dielectric matrix ? Can we obtain **long-range** ordered nanostructures??

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